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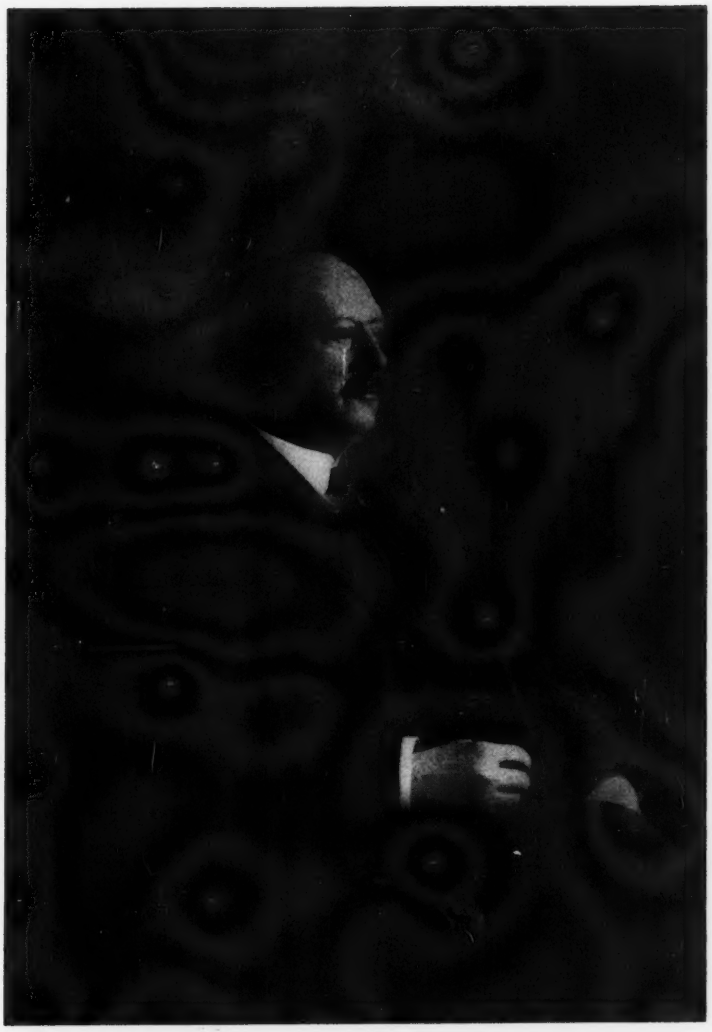

Ludwig Gattermann (1860–1921)

Contributed by Ralph E. Oesper, University of Cincinnati

(For further information about Ludwig Gattermann, see page 444.)

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Editor's Outlook

WE FEEL like apologizing for bringing up again the old issue of the effective use of trained scientific and technical personnel in the war. Nevertheless, it is one of the most important issues confronting us, and worth keeping before the public attention. And two important reports have appeared recently which merit summarizing.

The first of these proceeds from the War Policy Committee of the American Institute of Physics and urges the Army, Navy, and War Manpower Commission to take effective steps to insure the best use of the insufficient number of trained physicists in the war effort. Steps suggested include establishment of government-sponsored teacher training courses, adoption of wise occupational policies by the Selective Service System, provision of financial aid to well-qualified students, and use of physicists in the Army and Navy only for work requiring their training. There is nothing here which has not already been said repeatedly by the chemists.

But more fundamental than this is a report of the Philadelphia Regional Committee on Science and Mathematics Teaching. This committee of 60 members constituted itself from the local representatives of State and National scientific organizations, and did a very thorough job of evaluating the future needs of the armed forces and industry, in numbers of trained men and women, as well as of the present sources of supply. Chemists are concerned, of course, as one group of several. We think the greater portion of the findings and conclusions of the Committee are worth quoting, as follows:

FINDINGS

Facts substantiated our fears. Authoritative opinion and fact confirm the following statements:

1. The armed forces and industry need vast numbers of young men and women who have a thorough knowledge of mathematics up to and including trigonometry, and at least one year of physics, but few can meet the requirements.
2. Many high-school graduates and even college graduates have not taken some of these courses; others who have cannot use their knowledge without well-organized review.
3. Science teaching in many districts is substandard because of inadequately trained teachers or poorly equipped laboratories, or both.
4. There are not enough capable teachers to meet the demands for training the vast numbers of young people needed in the armed forces and industry.

RECOMMENDATIONS

With a sobering realization of the difficulties involved, but with the encouraging knowledge that in many communities great strides were being made we recommend that:

1. Mastery, not "passing," be the goal of teaching and learning.
2. Standards be maintained or increased, specifically in these items:
   - *a.* Colleges raise their standards in preparing teachers of science and mathematics.
   - *b.* State departments of public instruction require adequate instruction to the extent of maintaining and raising requirements for certification of teachers.
   - *c.* Promising undergraduates be encouraged to enter the teaching field and to take additional courses in science and mathematics during the summer.
   - *d.* Teachers of all subjects who have had training in science and mathematics be urged to qualify themselves for certification in these fields. Teachers already qualified be urged to take refresher and advanced courses. Where necessary, federal aid be sought for such training.
   - *e.* Special subsidies be sought to set up and equip school science laboratories where such laboratories do not exist.
3. Curricula be strengthened along the following lines:
   - *a.* All basic mathematics and other courses essential to pre-induction training be immediately made an essential part of the school curricula and be recommended for pupils able to profit by them.
   - *b.* High-school graduation requirements be revised immediately to permit and encourage every capable pupil to take algebra, geometry, trigonometry, and physics.
   - *c.* Pupils be given an opportunity to change their selection of subjects to be followed in the fall of 1942 so that additional emphasis may be placed on science and mathematics.
   - *d.* Provision be made for those pupils who desire to obtain mastery of subjects in which they are deficient and also for those who want more training in mathematics and science than is now possible in average classroom work.
   - *e.* Graphic and practical problem material be introduced continually into existing courses to direct pupil-thinking toward current military, technical, and scientific activities.
   - *f.* Adequate steps be taken to inform pupils, parents, and school officials of the importance of scheduling these essential subjects and of adopting a more serious attitude toward study.
4. Qualified teachers be urged to notify the proper school authorities of their readiness to assist, on a volunteer basis if necessary, in the preparation of trainees.
5. The War Manpower Commission and Selective Service authorities be informed of the imperative need of maintaining and increasing teaching forces and student groups in these fields to permit continuous implementing of the military and industrial establishments.

ELSEWHERE in this issue (page 445) will be found an announcement of the Federal loan fund for scientific and technical students. Although the provisions for the plan are not all that had originally been hoped for, they will go a long way toward making the "accelerated" college programs successful. It had been gloomily predicted that these accelerations would never get going unless government money was provided to pay the extra costs, both to the institution and to the students who would thus be cut off from their summer vacation sources of income. The general success of these programs this summer shows that such predictions were ill founded. Nevertheless, it is clear that

(*Continued on page 428.*)

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Nerve Gas on Tap

FRANK BRESCIA *College of the City of New York*

THIS WAR is not only a battle of bombs and of governments. It is also a battle of nerves—low brow for high brow psychology. The supposed use of nerve gases by the Germans, recently echoed to us, is an excellent illustration of a phase of the war of nerves conducted for the expressed purpose of reducing combat and civilian morale to the point where panics ensue or the desire to fight is lost.

Newspaper and radio discussions of "nerve gases" found their origin in the extremely rapid capture of Fort Eben-Emael (Belgium), May 10, 1940, and the success of the German Army in its recent offensive against the Crimea region.

Studied from a technical or a real point of view, the systemic or nerve toxics are revealed to be a fifth and unimportant class of the war gases. The vesicants, lung injurants, sternutators, and lacrimators are the four main classes. Physiologically, the systemics do not attack a particular organ or part of the body but rather are absorbed into the blood stream, death resulting from paralysis of the central nervous system. Illustrations of such gases are hydrocyanic acid and the cyanogen halides. These are generally known as cyanides. Phenylcarbylamine chloride, predominantly a lung injurant, is also capable of producing dizziness. These gases made their war debut July 1, 1916, during the battle of the Somme under the sponsorship of the French. Although, as a class, the systemic toxics are believed to be the most virulent poisons known, their physical properties render them impotent in the field. They are the least persistent of all war gases and in spite of the fact that the French alone used over 4000 tons of hydrocyanic acid, the facts show that extremely few casualties resulted. Briefly, we emphasize that nerve gases are well known but they are also known to have little, if any, tactical value.

But, the rumor boys and civilian generals are convinced that the Germans possess a "new nerve gas." How else do you explain the capture of Fort Eben-Emael? In a sense these "jerks" are correct. The Germans do have a "new nerve gas." It is remarkable in that you produce it yourself. You may mentally produce it, if you choose to believe the enemy does possess such a gas. Paralysis of the mind may be induced by a fear of the unknown, the unknown in this case being the possible existence of a combat agent unknown to anyone but the Germans. If your mind is really convinced through repetition that the allied soldiers were helplessly dazed by gas then it becomes psychologically possible to blow any kind of gas (or hot air) into your face and merely the thought that it is a nerve reactant will produce a sense of dizziness. Also, the fear of the existence of such agents, if sufficiently "advertised," may so overcome an individual that he is rendered useless for combat or any other type of service. For all practical purposes, he is a casualty.

Knowledge is the antidote for fear. With full understanding and appreciation of the manner in which Fort Eben-Emael was captured, mental apprehensions are reduced to a minimum.

The seizure of this citadel really demonstrates the weakness of the Belgians rather than the strength of the Germans. A brilliant plan (strategy) daringly executed (tactics) resulted in the surrender of the fort's crew. Modernized and heavily armed with artillery and anti-tank guns, the fort was designed to withstand heavy bombardments and to defend itself against concerted attacks even from long distances. This inaccessible mistress of might sat on the Albert Canal. Her specific mission was to cover the Albert Canal and as an integral part of the first line of the Belgian fortifications her purpose was also to prevent enemy passage across the Meuse River.

The strategy of the attack was not classical–artillery and aerial bombardment for several days followed by waves of tank-supported infantry troops. Rather, three separate but small paratroop groups were specifically assigned to neutralize the fortifications in question. One such group of 70 men reached its superstructure and in spite of its heavy defensive works, there were no weapons for protecting the superstructure with fire against anyone attempting to mount it. With high explosives, this group worked with surprising celerity and destroyed all turrets and guns in the upper casemates within ten minutes. Such internal high explosive charges are sufficient to stupefy people not otherwise killed or injured. The modern aerial land mines are also capable of producing similar effects. The chemical products of such explosions include approximately 60 per cent carbon monoxide and 2 per cent hydrocyanic acid, both of which possess systemic characteristics.

Concurrently, another patrol unit of 28 motorized demolition engineers approached through blind spots, seized the lower casemates, and exploded out the entrance to the fort. When the attackers from below and from above finally made contact, the remaining 800 members of the original crew of 1200 surrendered and were taken prisoners. Thus, 70 hidden men and a vanguard patrol captured the main unit of the Belgian defenses by the "insect technique." As a militarist expressed it: "It could be compared to an elephant hunter stationed in the forest who, confident of his powerful weapon, watched through a peep hole of his hiding place for his gigantic enemy to appear. But the pachyderm had arranged with a swarm of mosquitoes and just when the hunter thought himself

(*Continued on page 414.*)

The Nascent State

J. H. REEDY and E. D. BIGGERS *University of Illinois, Urbana, Illinois*

THE THEORY of nascent action is still in considerable vogue in classroom instruction. It is presented so casually that many students accept it as well authenticated, and are surprised when they hear that many authorities reject it.

The term "nascent state" is derived from the Latin *status nascens* (or *status nasciendi*), and Mellor (*1*) gives Laurent credit for introducing the term in 1846. It has certainly been in use for a longer time. Davy (*2*), in his Bakerian lectures of 1806 and 1807, refers to "nascent hydrogene" and "nascent oxygene."

THEORIES FOR ACTIVE MODIFICATIONS

A number of theories have been proposed to account for the peculiar activity of the nascent state. The one most generally accepted attributes it to the presence of free atoms. These atoms, by reason of their unsaturated valences, are very reactive, and combine vigorously with other substances. In the absence of anything else, they combine with each other, forming diatomic molecules. As a result of their activity, the life of these atoms is very brief, and the reagent loses its activity upon heating or standing. The development of this form of the theory is not easy to trace. A very clear statement appeared in Wurtz's book, "The Atomic Theory" (*3*), published in 1875, but, to say the least, it was foreshadowed by earlier writers.

Nascent Hydrogen. The doctrine of the nascent state has been developed, for the most part, in terms of hydrogen. Davy (*4*) noticed in 1807 that electrolytic hydrogen will combine with nitrogen in the presence of water, while ordinary hydrogen will not. Later it was shown that hydrogen formed by the action of active metals on solutions of non-oxidizing acids is a stronger reducing agent than ordinary gaseous hydrogen. For example, it will reduce Fe^{+++} ions to Fe^{++}, ClO_3^- to Cl^-, MnO_4^- to Mn^{++}, and so forth.

In 1853 Osann (*5*) proposed that nascent hydrogen was an allotropic form of ordinary hydrogen. From a supposed similarity to ozone, he assumed that it was triatomic and called it "ozonwasserstoff." A gaseous form of trivalent hydrogen was discovered by J. J. Thomson (*6*) in 1913 when canal rays were passed through hydrogen at low pressures. Wendt and Landauer (*7*) activated hydrogen by bombardment with alpha rays and by electric discharges. They thought that the product was triatomic and called it "hyzone." Paneth (*8*) reported that triatomic hydrogen probably exists as the ion H_3^+, and not as a neutral molecule.

Langmuir (*9*) prepared atomic hydrogen in the gaseous form in 1914 by passing ordinary hydrogen through an electric arc. The diatomic hydrogen was dissociated into the monatomic form in amounts varying with the pressure. This gas is very reactive, and shows marked reducing action. The life of the particles is very short, estimated in fractions of a second. If an aqueous solution of this gas could be prepared, it would probably show all the properties of nascent hydrogen.

One of the first definite challenges to the theory was by Tommasi (*10*) in 1878. He pointed out that the properties of nascent hydrogen were not definite, but that its reducing action varied with the source of the gas. To illustrate, the hydrogen evolved from sulfuric acid by zinc will reduce ClO_3^- ions to Cl^-, while the hydrogen evolved from water by sodium amalgam is without effect. Tomassi attributed these differences to differences in heat content; that is, the hydrogen displaced from acids by zinc was hotter (!) than the hydrogen from most other sources.

Other theories have been advanced to explain the variable energy content of the nascent gas. According to Ostwald (*11*), the hydrogen is liberated first as minute bubbles. The surface energy in these minute bubbles is enormous, and supplies the extra energy involved. A number of experiments might be cited in support of this view. For example, Zenghelis (*12*) reported that hydrogen diffusing through filter paper showed a reducing action on mercuric chloride solution. An inference from this theory is that the hydrogen bubbles displaced by zinc must be smaller (!) than those from less reactive metals. Bodländer and others explained the increase in activity as due to the occlusion of the hydrogen on the metal in the atomic state. The reducing power of the nascent hydrogen should therefore vary with the heat of occlusion on the metal involved. Bertholet (*13*) assumed that the reactants form primarily a *système réducteur* of variable energy content, and the nascent hydrogen is a product of a secondary reaction.

W. A. Noyes (*14*) and others have suggested that certain diatomic gases may have polar structures; *e. g.*, H^+—H^-, Cl^-—Cl^+, etc. These gases are supposed to dissociate into positive and negative ions, as $H^+H^- \rightleftarrows H^+ + H^-$. The H^- ion thus obtained is a powerful reducing agent, since it may lose two electrons and form the ordinary cation, H^+. Similarly, Cl^+ would be a powerful oxidizing agent, gaining two electrons to form Cl^-. Fry (*15*) in 1914 suggested that these electromers might be identical with the active particles in nascent reactions, and Pinkus (*16*) has more recently elaborated this concept into a general theory of nascent action.

Probably the strongest evidence in favor of the atomic theory of nascent action is the activation of hydrogen by contact with colloidal platinum or palladium. The gas appears to be adsorbed in the diatomic

form and to be desorbed in the monatomic form. The latter is probably identical with the electrolytic hydrogen formed when hydrogen ions are discharged on platinum or palladium cathodes.

None of these theories takes into account the effect of the nature and the extent of the surface of the solid. It is well known, for example, that powdered zinc is far more effective as a reducing agent than the same weight of zinc in massive form. This suggests that the reaction is not really homogeneous, but has a two-phase mechanism. This might be called a contact theory, the speed of the reaction depending, among other things, on the speed of diffusion of the solute and the effective area of the solid.

Nascent Oxygen. References to nascent oxygen in chemical literature are not as frequent as those to nascent hydrogen. Occasionally solid oxidizing agents (*e. g.*, manganese dioxide, bismuthic acid, etc.) are referred to as giving off nascent oxygen. Since the oxidizing strength varies from case to case, it hardly seems that atomic oxygen could be involved in all cases.

Marked oxidation effects are obtained upon anodes at which oxygen is being evolved. The intensity of the effect varies with the material of the anode, the overvoltage, etc.

Various mechanisms have been proposed for anodic oxidations. Besides the formation of atomic oxygen, a popular concept is the transfer of electrons from the reducing agent to the anode, followed in some cases by hydrolysis of the oxidation product.

Langmuir (*17*) in 1915 formed atomic oxygen by passing oxygen over electrically heated filaments at very low pressures and the temperature of liquid air. The preceding year, Koenig and Elöd (*18*), in their study of active nitrogen, postulated the existence of atomic oxygen, so as to explain some of the properties of active nitrogen. This active form of oxygen has a very short life, and no data on its solubility in water have been published.

Some interesting cases of contact effect in oxidation (*19*) have been reported. Indigo, potassium iodide, and carbon monoxide have been found to be oxidized by free oxygen, using hydrogenized palladium as a catalyst. Sodium arsenite is oxidized to sodium arsenate by oxygen in the presence of sodium sulfite. Similarly certain biochemical oxidations are induced by enzymes or oxidases. It is simpler to think of the inductor in these cases acting as an oxygen carrier, since there is no evidence that atomic oxygen is involved.

During the slow oxidation of certain substances (*e. g.*, phosphorus, turpentine, etc.) hydrogen peroxide or ozone is formed. This led Hoppe-Seyler (*20*) in 1878 to suggest that one atom from the oxygen molecule combines with the reducing agent, and the other is liberated in a nascent condition, and is thus free to combine with any second substance that may be present. On the other hand, Traube (*21*) held that the oxygen came from the water present, and that hydrogen peroxide was formed by the union of the residual hydrogen with the gaseous oxygen, forming hydrogen peroxide. Thus nascent hydrogen, instead of nascent oxygen, is evolved.

It will be noted that the mechanisms involving nascent oxygen are based on theoretical, rather than experimental considerations.

Nascent Chlorine. The earlier chemists thought that gold was insoluble in chlorine. This made it necessary to assume the existence in aqua regia of some extra-active ingredient that would account for the solvent action. This assumption later turned out to be unnecessary, for it was found that gold, while not attacked by carefully dried chlorine, reacts readily with chlorine water. Nevertheless, the misconception seems to have been largely responsible for the development of the doctrine of nascent chlorine.

While it cannot be disproved, the existence of nascent chlorine seems hardly probable. The behavior of aqua regia is very indefinite. Its activity is subject to many influences, particularly composition and temperature, and cannot be explained on the basis of a single solvent. More probably two effects are involved—oxidation and complex formation. The first effect is responsible for the variations that have been noted in the reactions of aqua regia. According to N. A. E. Millon (*22*), the presence of nitrous acid is necessary for vigorous action. The particular effect of nitrous acid probably lies in the fact that it is a much more vigorous oxidizing agent than nitric acid of the same concentration, and therefore exerts a stronger effect in such reactions as the following:

$$Au + 3H^+ \rightleftarrows \begin{cases} 3H \begin{cases} \xrightarrow{3HNO_2} 3NO + 3H_2O \\ \xrightarrow{HNO_3} \text{Little effect} \end{cases} \\ Au^{+++} \xrightarrow{4Cl^-} AuCl_4^- \end{cases}$$

It has been known since the beginning of the last century that, while chlorine and hydrogen do not combine in the dark, the action proceeds rapidly under the influence of light. The phenomenon suggests that one or both of the gases may be "insolated"—that is, activated by light. Draper (*23*) studied the reaction in detail in 1841–45, and noted, among other things, that the gaseous mixture undergoes an increase in volume just at the beginning of the reaction (the "Draper effect"). The effect of light on chlorine has been studied by many investigators. Favre and Silbermann (*24*) reported that illumination increases the heat of reaction when chlorine is absorbed by potassium hydroxide. A large number of patents have been issued covering the claim that chlorine could be activated electrically, thereby increasing its chemical energy. On the contrary, Mellor (*25*) could detect no change in the ratio of specific heats on irradiating chlorine, and Vernon (*26*) and Briner and Durand (*27*) reported that chlorine showed no change in volume when subjected to a silent discharge. More recent investigators have come to the conclusion that the activation of chlorine by light may be due to other causes than simple thermal dissociation. Bodenstein and Taylor (*28*) and others have explained that the combination of hydrogen and chlo-

rine under the influence of light is a chain reaction, initiated by the quanta of energy supplied by the light. The reaction consists in successive steps, represented as follows: (1) Cl_2 + 1 quantum → 2Cl (activated); (2) Cl (activated) + H_2 → HCl + H; (3) H + Cl_2 → HCl + Cl (activated). The activated chlorine atom is thus cyclically regenerated, and the reaction may repeat itself until the chain is broken by contact with a glass surface or otherwise. In this way a single quantum of energy may be responsible for the formation of thousands of molecules of hydrogen chloride. The life of an activated chlorine atom is very brief; Bodenstein and Taylor estimated it at six-tenths of a second. This photochemical effect is limited to gaseous mixtures, and is not shown by chloride solutions.

Nascent Nitrogen. One of the first authentic cases of active gases was nitrogen. In repeating the work of some earlier workers, Strutt (*29*) found in 1911 that nitrogen which had been treated with an electric discharge at low pressure was more reactive than ordinary nitrogen. It would not react with oxygen or hydrogen, but it would combine with iodine or sulfur with blue flames; and also with certain hydrocarbons forming hydrogen cyanide. Strangely a trace of foreign matter is necessary for this activation; *e. g.*, oxygen, methane, carbon dioxide, hydrogen sulfide, mercury, etc. The speed with which active nitrogen returns to its normal state is relatively slow, compared to active hydrogen or active oxygen.

Strutt thought that active nitrogen is monatomic, though certain of its reactions are analogous to those of ozone and suggest that it might be triatomic. Trautz (*30*) argued that active nitrogen consists mainly of triatomic molecules which he called "nitrozone" or "triazone." Spectral analysis led Duffieux (*31*) to think that active nitrogen consists of ionized atoms, N^+, while Dhar (*32*) assumed ionized molecules, N_2^+.

THE SOLUBILITY OF NASCENT HYDROGEN

If it could be shown that actual contact between the reducing agent and the metal is not necessary, but that the reaction proceeds at a distance, the existence of the nascent reagent in a soluble form would be definitely indicated. On the contrary, if the reaction is limited to the surface of the solid, there is no need for postulating a superactive reagent. The process is then reduced to the very common heterogeneous type of mechanisms, in which the solid reacts directly with the solution. This consideration led to the following experiments, which were carried out with a view of determining whether these reactions could be detected out of contact with the metal.

The Reduction of Potassium Permanganate by Zinc. Various devices were tried to prevent contact of the metal and the permanganate. First a mat of glass wool was placed in the bottom of a glass cylinder, and covered with dilute sulfuric acid. A piece of granulated zinc was placed on top of the glass wool, and, by means of a thistle tube, a dilute solution of potassium permanganate was introduced below the acid. As the zinc dissolved, the permanganate diffused into the colorless solution above the glass wool, and in a short time the whole solution was decolorized.

The experiment was repeated, only a piece of parchment paper, cut to the size of the cylinder, was placed between the glass wool and the zinc. The reaction proceeded as before, but more slowly. Similar results were obtained when silica gel was substituted for the glass wool.

The general course of these experiments suggests strongly that convection currents were set up in the solution by the evolution of hydrogen gas, and that any nascent effects may have been masked completely by the stirring.

As a check on the diffusion of active hydrogen through parchment, platinum foil was used as the partition. The apparatus was improved by setting up two small cylinders end to end in a beaker, and separating them with a very thin platinum foil. The lower cylinder, which was closed at the bottom, was filled with silica gel impregnated with potassium permanganate. The upper one contained a piece of zinc. Dilute sulfuric acid was added to the beaker until the upper cylinder was covered. About two hours were required for complete decolorization of the permanganate. The presence of bubbles of hydrogen on the lower side of the platinum foil was evidence that some hydrogen had diffused through the foil. A peculiar effect was noted: the reduction of the permanganate proceeded upward from the bottom of the cylinder. In cases of low acidity, the upper surface of the silica gel was quite brown due to the formation of manganese dioxide, and the color faded out toward the bottom. Evidently diffusion was still operating to some extent.

The most conclusive test for a soluble form of active hydrogen was found in the following simple experiment: cold, dilute sulfuric acid was poured over granulated zinc on a filter paper in a Büchner funnel and was rapidly filtered by suction into a dilute solution of potassium permanganate. The permanganate, if present in sufficiently small amount, was completely reduced. Blank experiments made by filtering the acid through paper containing no zinc gave negative results. These filtrates lost their activity upon standing or heating. Filtrates of dilute sulfuric acid through zinc that had been treated with cupric sulfate seemed to show more marked reducing power than in the case of untreated zinc. In a similar way, the filtrates from solutions of finely divided aluminum or magnesium in cold dilute hydrochloric acid were found to have a slight reducing action on mercuric chloride solution.

It is admitted that these experiments are not conclusive proof of the existence of nascent hydrogen in a soluble form. The reducing effect might be due to hydrogen peroxide, formed in the reaction between zinc and sulfuric acid in the presence of air. However, solutions of hydrogen peroxide in sulfuric acid-zinc sulfate were found to be more permanent than these filtrates. Any reducing action of the filter paper was eliminated by using a mat of asbestos.

Reducing Action of Active Hydrogen. The possibility of the identity of the active hydrogen of Langmuir with nascent hydrogen suggested the following experiments:

A 100-watt tungsten electric lamp was tapped with two tubes, one at the side and the other at the tip. A current of hydrogen was passed through the bulb and, after the air had been displaced, the filament was heated to incandescence by a 110-volt current. The effluent gas was bubbled through an acidified solution of potassium permanganate. Since active hydrogen is known to have a very short life, the distance between the filament and the solution was made as short as possible. After continuing the experiment two hours, there was no perceptible change in the color of the solution.

The experiment was repeated, this time passing the current of hydrogen through an electric arc from a high potential transformer. After a short time the permanganate was completely decolorized. Ceric sulfate was also reduced in this way, using orthophenanthroline as an indicator. The possibility of direct reduction by gaseous active hydrogen was eliminated by saturating water with the gas, and later adding the permanganate solution. Reducing action was always indicated, though in small amount.

Active oxygen, prepared by passing oxygen through the electric arc, showed a similar heightening of activity. A ferrous solution was rapidly oxidized to the ferric state.

These experiments indicate that nascent hydrogen may be operative in the above reductions, but only to a slight extent. The dominant reaction appears to take place at the surface of the solid, and depends upon the oxidizing agent being supplied by diffusion and convection.

SUMMARY

There are conflicting opinions with regard to the nature of nascent action. These opinions are based largely upon theoretical considerations and, for the most part, are not susceptible of experimental proof.

The following evidences support the theory of free atoms in nascent action:

1. Electrolytic hydrogen is much more reactive than ordinary hydrogen.
2. Ordinary hydrogen is activated by contact with colloidal platinum or palladium. Presumably it is first adsorbed as diatomic hydrogen and desorbed as monatomic hydrogen.
3. Atomic hydrogen formed by the thermal dissociation of ordinary hydrogen seems to have the properties needed to account for nascent action.
4. The active form seems to have a very slight solubility in water, as evidenced by diffusion through permeable materials and a brief persistence after filtration.

The principal reaction in the so-called nascent phenomena appears to be a contact reaction. This is evidenced by the following considerations:

1. The behavior of nascent gases is not constant, but varies with the solid evolving it.
2. The interposition of permeable materials between the active solid and the solution removes the nascent effect almost completely.
3. Active contact between the solid and the solute seems to be necessary to account for the principal effect.
4. The effect is influenced strongly by the nature of the surface of the solid.
5. Convection currents appear to be sufficient to obviate any need for diffusion of the active material.
6. It is not probable that monatomic gases would be soluble enough to account for the over-all effect.
7. Excepting certain reactions of hydrogen and nitrogen, most nascent reactions can be explained by the simple transfer of electrons.

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The glycerine produced as a by-product in making ten pounds of soap is the amount required for manufacturing six pounds of dynamite.

A Grating Spectrograph for Use in Qualitative Analysis

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IT IS not only good pedagogy for the student of qualitative analysis to confirm his results by an entirely independent method of procedure and thereby establish confidence in his technic, but also very instructive to acquaint him with the capacities and limitations of the spectrograph as an analytical tool. Unfortunately, good commercial spectrographs are expensive; and most of them are too complicated for the average student to manipulate without risk. But there is a new design of grating spectrograph which eliminates both objections. It is manufactured by Adam Hilger Ltd., of London, under the name "Technal," and, while no less expensive than other good grating instruments, it has exceptional properties of ruggedness and simple design which are so inherent as to be preserved even when homemade by relatively inexpert hands.

It is not the purpose of this paper to give explicit directions for the construction of the "Technal" spectrograph. Homemade instruments are usually the result of whatever happens to be lying around plus a few deliberately purchased parts. For this reason no two are ever quite alike. But having the mechanical principles well in mind, it is possible to build a modest version of the "Technal" spectrograph in about two weeks of evenings. Its cost will vary, of course, depending upon the selection of material in one's junk boxes and the degree of refinement to which the design of the instrument is carried. But in no case should the cost exceed fifty dollars. Half this amount should be adequate.

The "Technal" mounting is the most recent of the "minimum astigmatism" mountings for the concave grating. Others are the Wadsworth and the Eagle mountings. Both of these last are composed of relatively delicate mechanical and optical parts, while the "Technal" is not only simple to understand and operate, but rugged enough to withstand almost any kind of ordinary abuse.

First let it be made clear why the concave grating is preferable to the more familiar prism as a dispersing medium. Prisms introduce irrational dispersion—non-uniform separation of equal wave length intervals in different spectral ranges—which makes the interpretation of spectrograms unnecessarily difficult for the beginner. Furthermore, the prismatic instrument must always contain three component parts—the collimator, prism, and camera, each of which involves at least one pair of optical surfaces. For analysis in the ultra-violet range these parts must be made of quartz, which is very expensive. The grating spectrograph, on the other hand, not only produces linear dispersion but may contain no lenses whatever and only one spherical reflecting surface if the concave grating is employed. With these an aluminized reflecting surface is all that is required for efficient operation in the ultra-violet. This simplicity carries a twofold advantage: it reduces the initial cost of the instrument and makes it easier to keep in adjustment. Another advantage in the use of grating dispersion is the wide range of dispersions available in the higher orders of spectra. While the intensity of these higher orders is usually considerably less than that of the first order, the high intensity of the carbon arc, which is almost invariably used for qualitative analysis of non-conducting samples, allows them to be used for more precise analysis of the complex spectra characteristic of the transition group of elements. The ultra-violet range of the second order spectrum overlaps the visible range of the first order in grating dispersion, but when the first order is being photographed the ultra-violet of the second order may be filtered out completely by means of a plane-parallel strip of soda glass just before the plate at this point. The concave grating does possess a few disadvantages, of course, the worst of these being astigmatism. But this too can be effectively controlled either by means of properly designed slit illumination systems, or by employing the minimum astigmatism mountings, of which the "Technal" is an example. These reduce the stigmatic error to such a small figure that it becomes unimportant in the normal working ranges.

THE "TECHNAL" DESIGN

The "Technal" design has no inventor's name associated with it as yet, but J. S. Dowell of Adam Hilger Ltd. has described the mounting and the Hilger interpretation of its design,[1] which he credits to Cotton[2] and Richards.[3]

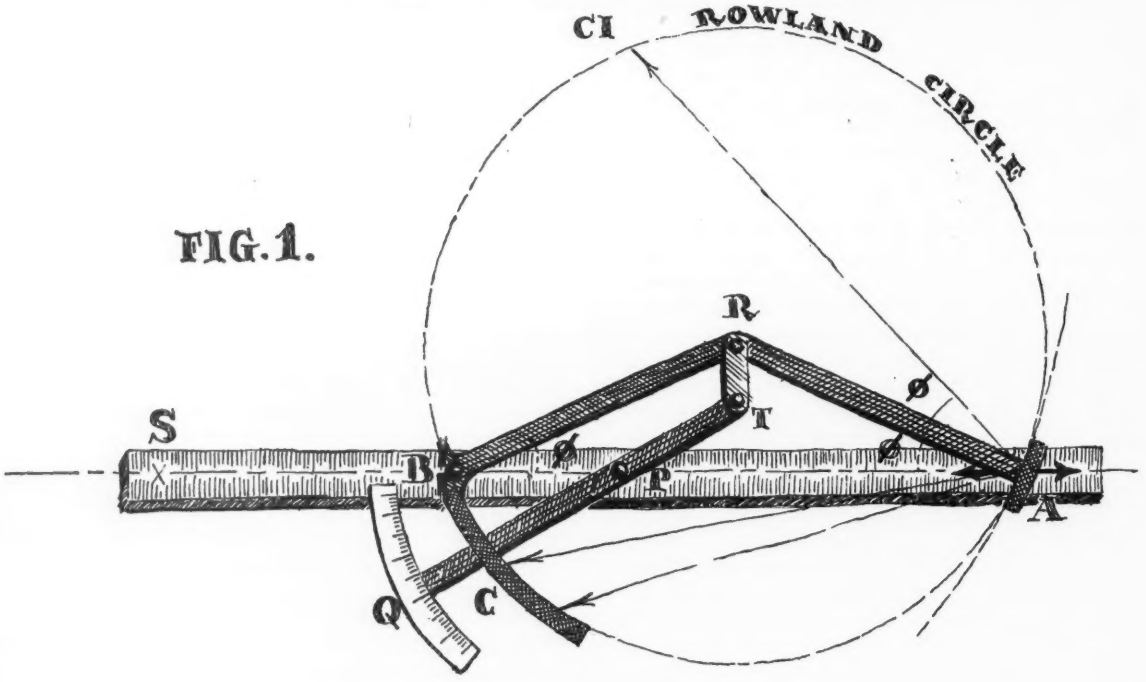
The mechanism involves only three levers of fixed length, a pivoting hinge, and a short track along which the grating moves under control of the lever system. The arrangement of parts is shown diagrammatically in Figure 1, the grating being at A, the slit at B, and the plate at C. The line BA represents the center line of the spectrograph bed and the levers BR and AR are in

[1] DOWELL, *J. Sci. Instruments*, **17**, 208 (1940).
[2] COTTON, *Compt. rend*, **186**, 192 (1938).
[3] RICHARDS, *Proc. Am. Phil. Soc.*, **51**, 554 (1912).

length one-half the radius of curvature of the grating and have the grating and slit-plate elements rigidly fixed to their ends. Where they meet at R they are pinned together so as to articulate. A track which is parallel to the bed BA is placed under A, and is long enough to allow the grating element on the radius arm AR to travel along the bed BA in the direction of the double ended arrow for a few inches. It is evident, since BR and AR are radii of the Rowland circle of the grating, that by moving the joint R toward or away from the line of the bed AB the range of wave lengths recorded on the plate C will change. Furthermore the parts will always remain on the circumference of the Rowland circle and will therefore be in correct focal relation to each other at all times. If a light source is located at S on the line of the bed AB prolonged, the incoming light ray must always fall fully upon the grating at A no matter what wave length range is being photographed. If R is moved away from the bed it will be found that the plate will record the longer wave lengths or higher orders of dispersion of the grating since the central image CI of the slit is on the opposite side of the radius arm AR at an angle 2ϕ with the bed. The angles ϕ are all equal, as is evident from the geometry of the mechanism. They usually have values ranging from 0 to perhaps 10 or 12 degrees.

The angles ϕ are varied by moving the joint R from outside the instrument by means of the lever QPT which is pivoted on the bed of the instrument at P and connected with the joint R by a short toggle RT. The pivot is somewhat nearer T than Q in order to provide a small mechanical advantage and greater precision of motion of R. The outer end Q of the lever sweeps a scale upon which the wave length ranges for each setting are marked. Not more than half a dozen standard settings need be marked upon the scale. They may be determined by experiment after the instrument is completed and in final adjustment. It is evident that, once adjusted, the entire optical system is completely controlled by the motion of the lever QPT and with complete assurance that all optical parts are properly oriented with respect to each other for perfect focus. Indeed it is difficult to make them behave otherwise. It is this feature which makes the "Technal" design so superior for student use.

FIG. 1.



As for astigmatism: all images formed by a concave spherical surface suffer astigmatic distortion except that one image which falls exactly in line with the light source. Astigmatism increases slowly at first as one travels from this point in any direction in the focal plane, but increases rapidly beyond angular departures which are in excess of a very few degrees. Those lines nearest the slit will be most nearly stigmatic and those farther away will show increasing distortion. It is for this reason that the slit in the "Technal" mounting is placed as close to the ultra-violet end of the plate as possible. Since the far ultra-violet sensitivity of plates is always somewhat lower than that of the near ultra-violet and visible blue it is desirable that no light should be wasted in that region. Ideally, of course, the slit should be placed in the very center of the plate, but this is difficult mechanically and would cause great incon-

venience in operation. The "Technal" arrangement has proved to be quite satisfactory, even without special precautions to stigmatize the optical system by means of auxiliary lenses or mirrors in front of the slit. Should increased stigmatism be necessary, however, the methods of Sirks[4] and Baly[5] may be employed.

When the carbon arc is used as the light source it has been found that a quartz lens of 10 to 15 cm. focal length focused to project an enlarged image of the gas column on the slit renders the incident light sufficiently parallel for a Hartmann diaphragm or rotating logarithmic sector to be used in front of the slit.

For spectrochemical analyses of compounds containing iron or other elements of the transition group which have exceedingly complex spectra, two minimum specifications must be observed regarding the dimensions of the optical system of the spectrograph: (1) dispersion of at least 16 A. per mm. and (2) sufficient resolving power to separate completely two lines of equal intensity not more than 0.4 A. apart. In grating instruments this requires a focal length of about one meter, 15,000 lines to the inch, and a ruled surface at least 30 mm. wide. The Central Scientific Company of Chicago sells a Wallace replica grating having these minimum specifications for a little more than ten dollars. These gratings are of fairly good quality initially but may be improved by changing the shape of the factory-made mask to be somewhat longer, thereby exposing more ruled surface and increasing the resolving power, and somewhat narrower, in order to compensate for the irregularities in the collodion replica. The precise shape of the mask must be determined by experiment. It is a long and exasperating job but eminently rewarding in the end.

CONSTRUCTION

The slit and the plateholder are the most difficult parts of the instrument to construct and should be given double their share of careful planning and workmanship. A fixed slit of moderately narrow width is to be recommended. The plate must be curved to the circumference of a circle whose radius is one-half the radius of curvature of the grating—the Rowland circle. Naturally it is more than one can expect of glass plates to bend to fit the circumference of a half-meter circle, therefore cut films must be used with these instruments. The "plates" may be strips of 35-mm. motion picture film if it is expected that only one or two samples will be run at a time; or 8 × 10-inch cut film sliced down the middle to the standard spectrographic size 4 × 10 if more extensive work is anticipated. On these 4 × 10-inch plates it is possible to record at least sixteen well-separated spectra with their iron comparisons. The spectra need not be more than three millimeters high if no comparison spectra are juxtaposed, but should be half again as high with comparison spectra so that about one millimeter of the end of each line can interfinger with the comparison lines. This simple device increases the accuracy of plate measurement, since lines of nearly the same wave length are more easily classified as coincident or separate.

The astigmatism of gratings causes the ends of the spectral lines to be ragged in appearance, the brightest

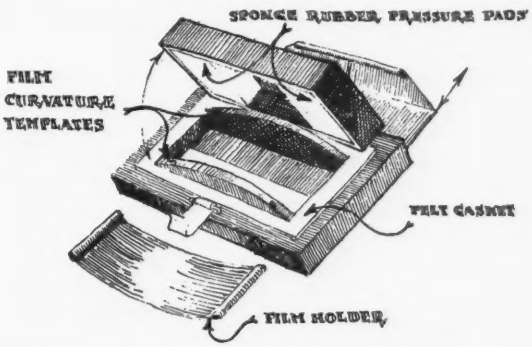


FIG 2. PLATE HOLDER

line being longest. In order to conserve plate space and trim up the spectra it is necessary to build an exit slit just in front of the plate in its holder. This slit is at right angles to the principal slit of the instrument and is preferably constructed to have variable width. The slit's function is simply to limit the height of the lines and make their outer terminations sharp. A pair of brass-edged foot rulers is admirable for the purpose They may be made adjustable by coupling the two at their ends in the manner of the navigator's parallel rule.

The light-tight housing around the optical parts of the instrument may be made of sheet metal or of plywood screwed to a light wooden frame. The housing should have a door or hatch in it near the grating end of the case so that the grating is accessible for adjustment whenever necessary. A simple flap shutter placed in front of the slit but behind the Hartmann diaphragm is a convenient accessory. The plate holder motion scale will be found to be more useful if it is graduated in metric units. The metric scale of a 6-inch celluloid pocket ruler glued to the plate holder track with cellulose acetate cement serves admirably.

The design of the bellows between the light-tight housing and the articulating plate holder track presents something of a problem. Spectrograph bellows are usually of such an odd size and shape that they must be specially made. Bellows cloth costs about one dollar per yard. Bellows may be installed in the usual accordion pleat fashion built up of two layers of bellows cloth with cardboard stiffening pieces cemented between—rubber cement is recommended—or since the span is always very short, simply cut to fit the gap and allowed to fold as it will without reinforcement inside. The

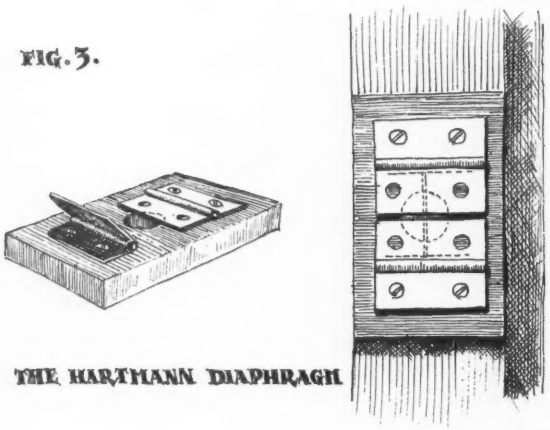
[4] SIRKS, *Astron. and Astrophys.*, **13**, 763 (1894).
[5] BALY, "Spectroscopy," Longmans, New York City, **1924**, Vol. 1, pp. 165 ff.

latter is quite satisfactory for small instruments, the natural stiffness of the cloth itself being sufficient.

A rack and pinion control of the plateholder motion is a convenience which may be eliminated without impairing the efficiency or accuracy of the instrument.

The Hartmann diaphragm has been mentioned. For accurate comparison of two samples this device is absolutely essential. It may be constructed quite simply by means of two small brass hinges screwed to a panel with a hole in it just before the slit. When both hinges are opened flat upon the panel their leaves do not quite touch (see Figure 3). Thus when two samples are

FIG. 3.



THE HARTMANN DIAPHRAGM

exposed with one hinge open at a time, their spectra will overlap the same amount by which the hinges do not touch. The entire purpose of this arrangement is to permit two spectra to be photographed side by side without mechanical motion of any part of the spectrograph between exposures. This assures perfect optical juxtaposition so that if two lines continue unbroken across both spectra one may be sure they have the same wave length within the limits of error of the optical system.

When the inner mechanism of the instrument is complete, the entire inside of the case and the parts enclosed should be painted dead black. Ordinary blackboard paint is admirably suited to this job, containing enough varnish to stick equally well to metal and wood. Since the instrument is likely to be used in a dimly lighted room, the outside of the instrument is best painted a light gray so that it is more easily seen. It is convenient to mark the rulings on the plate holder motion scale with zinc silicate paint to which a trace of a uranium salt has been added. A dot of the same on the plate holder makes it far easier to set the plate holder without turning on bright lights in the room. Should the phosphorescent paint be too dim for ready visibility to those coming in from brighter quarters, a small argon night light may be used to excite the fluorescence temporarily.

A RECOMMENDATION FOR STUDENT USE OF THE INSTRUMENT

Since the purpose of the spectrograph is to check analyses made by the wet method it is suggested that the method of coincidences be used. This method employs the Hartmann diaphragm by exposing the sample first, and then, after reversing the hinges, the element which is thought to be present. If the element is present in the sample the lines of the element will be continuous across both spectra. This procedure is very accurate and requires a minimum of physical and mathematical knowledge on the part of the student. Indeed, it can be explained so as to require none at all, if the student is willing to accept his instructor's word without further proof, as most students are.

An alternative method may be desirable for making complete spectrochemical analyses. This method employs the iron comparison spectrum which is photographed, by means of the Hartmann diaphragm, in registry with the spectrum of the unknown. This pair of spectra may then be compared with a series of negatives of single elements, each of which has an iron comparison spectrum in registry beneath it. Since the iron spectrum is common to all, it is possible to perform an analysis by superimposing the spectra of the elements upon the spectrum of the unknown in such a way that the iron spectra on each coincide. Once registry is established the lines of the element will coincide with those in the unknown if the element is present in the unknown.

For advanced students, it may be desirable to perform the analysis by measuring the wave lengths of the lines in the spectrum of the unknown by interpolation from the iron comparison spectrum, and looking up the elements in a set of reliable wave length tables such as Kayser's, the Handbook of Chemistry and Physics, or M.I.T. tables. This is a time-consuming process even for an experienced spectrographer, hence the sample should contain only the simplest components to begin with, such as a feldspar (Na, Ca, Al -silicate) or a mixture of alkali salts.

It is a common misapprehension that the spectrographic test is the ultimate in sensitivity for all the elements. In order to acquaint the student with the variable sensitivity of spectrochemical tests in different portions of the periodic table it is instructive to let him take spectra of several elements throughout the periodic table. Tests for the alkali metals are exceedingly sensitive; for the transition elements fairly sensitive; and for the amphoteric elements rather insensitive. The electronegative elements can be recorded only under special circumstances in the carbon arc. Fluorine, for example, can be recorded only when calcium is present in fair abundance, at which time it will yield a fairly strong CaF band head in the near ultra-violet. The noble gases, of course, yield emission spectra only when excited in high voltage discharge tubes under reduced pressure. Despite these limitations, the spectrograph will detect satisfactorily more than two-thirds of the elements in the periodic table.

The Mathematical Expression and Interpretation of Scientific Measurements

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NOTE: *The following paper is an attempt to condense the theory of errors and related topics useful to the laboratory technician into a concise, readable article, avoiding mathematical derivations, etc. It was prepared as a reference work and statistical guide for general distribution to members of this laboratory. Much of the material is usually available only by gleaning works on Statistics: this requires a knowledge of statistical terminology and symbolism.*

ERRORS AND SIGNIFICANT FIGURES

A TRUE value can never be absolutely determined by any measuring device. Thus, the length of a rod may be measured to within 10^{-2} cm. of the true value by means of a good rule. A vernier caliper might yield a reading within 10^{-3} cm. of the true value, while a good micrometer might permit of an estimate within 10^{-4} cm.

To generalize, instruments might be devised which will give readings differing from the true value by 10^{-n} cm., but so long as n is finite, the absolute true value itself cannot be ascertained.

Consequently there is always a finite difference between a determined value and the corresponding true value. This difference is referred to as an *error*. If this error is introduced solely through the limitations of the measuring instruments or senses of perception, it is referred to as an *accidental error*. If, on the other hand, it arises through a misreading or miscalculation, it is termed a *mistake*.

An error may be *determinate* or *indeterminate*. An example of the former would be an error introduced by a measuring instrument, which could be determined by calibrating the instrument with a superior measuring instrument. Determinate errors may be errors due to conditions, instrumental errors, errors in method, or personal errors. Accidental errors generally are indeterminate, and the theory of probability is used to cope with them.

Still another type of error is the error due to bias. An example of this would be an error arising through the attempt to evaluate a second reading to conform as nearly as possible with a first reading.

Precision is the term used to represent the degree with which a value is free from accidental error and therefore is a gage of the closeness of approach of a series of measurements of the same quantity. *Accuracy* is the term used to represent the degree of concordance between a given value and the true value of a quantity. It is commonly extended to mean the degree of concordance between a given value and the most probable value of the quantity. Although these terms are frequently confused, it should be obvious that a result may be unusually precise and yet highly inaccurate.

It is to be noted that the term "error" is very commonly used to denote the difference between the value of a single determination and what is calculated to be the most probable value. The more rigorous terminology for this quantity, however, is the "*residual* of the measurement."

If P be the most probable value and r be the maximum residual due to all the errors which might reasonably be suspected of occurring, then the true value might be said to lie most probably within the range $P \pm r$. This quantity r is referred as to the *absolute error*. The *relative or fractional error* is then defined as $\pm r/P$ while the percentage error is $\pm 100\, r/P$.

In practice, determinations are commonly expressed in the form $m \pm n$ where m is the measurement as read and n is the most probable error.

A *number* may be defined as an expression of a quantity. A *figure* or *digit* is any one of the characters: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, which, alone or in combination, serve to express numbers. A *significant figure* is a digit which denotes the amount of the quantity in the place in which it stands and is any one of the digits, except 0, when it is used merely to designate the position of the decimal point. Thus, the number 437.02 has five significant figures; 0.00012 has two significant figures, as has 0.12×10^9. However, a number such as 1400 gives no clue as to the number of significant figures, since the last two zeros may or may not be significant. In such cases a direct statement must be made. Note, on the other hand, that 1400.0 implies five significant figures.

A number is said to be *rounded* to n significant figures when all digits to the right of the nth place are discarded. To round a number to n significant figures with minimum error, the following procedure is accepted:

1. If the number to be discarded is greater than half a unit in the nth place, increase the digit in the nth place by 1.
2. If the number to be discarded is less than half a unit in the nth place, do not alter the digit in the nth place.

In the event that the discarded number is exactly half a unit in the nth place, there are two generally accepted procedures:

1. Increase the digit in the nth place by 1.
2. Do not alter the remaining number if the digit in the nth place is even, but increase the digit by 1 if it is odd.

For example, in rounding off the numbers 23.45 and 23.75 to three significant figures, the results would be 23.4 and 23.8.

Of these two methods, the latter is generally most conducive to minimum error, since the errors are not consistently cumulative, but may tend to neutralize each other. Other procedures might be always to leave the digit in the *n*th place unaltered; or to increase it by 1 if it is even, and not alter it if it is odd. All these methods are, of course, arbitrary.

The usual procedure in laboratory work is to round off values so that only the last significant figure is in doubt. Thus, if measurements of a quantity should be 105.6, 104.4, and 105.2 and the average be desired, the sum 315.2 would be divided by 3. This would give an answer of 105.0666 . . . . Since the figure in the tenths place would be doubtful, the number would be rounded off to this place. The division, however, would need be carried to the hundredths place, in order to know to what figure the digit in tenths place should be rounded. Thus, the answer would be 105.1. A number such as 105.07 or 105.067 would give a false appearance of accuracy. Should the first doubtful figure of a quantity be 0, it should be so expressed, since a buret reading of 37.30 expressed as 37.3 would give a false expression of the precision of the reading.

In making computations there are several rules for estimating significant figures. They are as follows:

Addition: If several quantities are added, the sum should contain *only* as many significant figures as the quantity having the greatest absolute error. Obviously, the error in the sum may be as great as the sum of the absolute errors.

Example: Add 23.1, 0.0121, 0.476, and 324. The answer added as it stands, is 347.5881. Since the quantity having the greatest absolute error has a potential error in tenths place, the answer should be expressed as 348.

Subtraction: This is perhaps the most generally misunderstood calculation in so far as the theory of errors is concerned. It is an operation which may lead to a great loss of accuracy. As an example of this, suppose 10,080 ± 45 is to be subtracted from 10,290 ± 45, where the maximum error in each case is 45. Subtraction gives: (10,290 ± 45) − (10,080 ± 45) = 210 ± 90. Of course, the two errors might cancel, but one can never be certain of this occurring and thus it is necessary to write the quantity indicating the maximum error.

The striking characteristic of this example is that, while the accuracy of the two given numbers is better than 0.5 per cent, the operation has given rise to a number with a potential error of nearly 43 per cent! Needless to say, calculations of this type should be avoided as much as possible.

Multiplication and Division: It can be proved that the relative error of a product or quotient may be as great as the sum of the relative errors of the numbers used in the calculation. It is conventional, therefore, to give a result to as many significant figures as are contained in the least accurate number entering into the multiplication or division.

INTERPRETATION OF MEASUREMENTS

A series of measurements made with the same degree of precision will commonly yield a series of differing values, due to the occurrence of accidental errors. The correct interpretation of these values is usually as important as the measurements themselves.

There are three values obtainable from a given series which are generally of interest and vary in usefulness according to the object of the measurements. They are the *mean*, *median*, and *modal* values.

The *mean* value (M), more rigorously, the *arithmetic mean*, but commonly referred to as the "*average*," is the value obtained by algebraically adding the members of the series and dividing by the number of terms. This value has two important properties:

(1) The algebraic sum of the deviations from the mean is zero.
(2) The sum of the squares of the deviations from the mean is a minimum. (*Cf.* the principle of least squares.)

If the series of measurements were written in order of increasing value, the value in the center of the column thus formed would be the *median* value (Mi). This value may be more rigorously defined as the value equaled or exceeded by exactly half the values in the given list, arranged in order of increasing value, and provided that the measurements are of the same degree of precision. In the event of a central pair, the median is usually taken as the arithmetic mean of this pair.

The most frequently occurring value or, more technically, the value about which the observed values cluster most densely is the *modal* value (Mo). This definition applies only for measurements made with the same degree of precision. The importance of this value is, perhaps, not so immediately apparent as that of the mean or median, but is well illustrated by the case of the clothing manufacturer who is little concerned with mean or median clothes sizes, but whose entire business success depends upon his knowledge of the modal sizes, *i. e.*, the sizes most commonly worn.

Although the modal value is not a mathematical concept, but rather a matter of frequencies, there is a *mathematical mode* which approximates the true mode and is defined by the relation: $Mo = M - 3(M - Mi)$.

The *mean error* of a series of measurements of equal precision is the absolute sum of the errors divided by the number of errors, *i. e.*, the arithmetic mean of the errors taken without regard to sign. Since the true errors are never known, this quantity can be approximated by computing the arithmetic mean of the residuals. The result thus obtained is known as the *average deviation* (a.d.) or *mean deviation*. When the number of measurements is small, the mean error is best approximated by the formula:

$$\epsilon = \frac{\Sigma|r|}{\sqrt{n(n-1)}}$$

where ϵ is the approximation, $\Sigma|r|$ is the sum of the residuals without regard to sign, and n is the number of residuals.

One very important use of the average deviation is in the rejection of doubtful measurements. When an individual measurement of a series differs widely from the other members of the series, it is likely to be the result of a mistake and is rejected before making cal-

culations. A good method for determining whether a value should be rejected is as follows: omit the doubtful value and compute the average deviation from the mean. If the difference between the mean and the doubtful value is greater than five[1] times the average deviation, the value should be rejected, since the probability of such a value occurring under conditions of normal distribution is less than one in one thousand. Indeed, a mean is sometimes taken after rejecting the lowest and highest quarter of the series. Such a value is known as a *midmean* (Mm).

Another very important computation is the square root of the mean of squares of the deviations. This quantity, known as the *standard deviation* (σ) may be expressed as follows:

$$\sigma = \sqrt{\frac{\Sigma(a_n - S)^2}{n}}$$

where σ is the standard deviation, $\Sigma(a_n - S)$ is the sum of the differences between the measurements and their mean value, and n is the number of measurements.

When a series of measurements are made with the same degree of precision, the differences are due to accidental errors. These errors are generally regarded as being of chance occurrence and treated by theory of probability. As with the classical coin-tossing and dice-rolling experiments, the observed occurrence of an event tends to approach the theoretically probable occurrence as the total number of events increases. The case wherein all events occur according to their theoretical probability might be referred to as an "ideal" case. An ideal case would then be approached as the number of events approached infinity.

If, in the ideal case, the frequency of occurrence of an error were plotted as an ordinate against its magnitude, as an abscissa, the well-known *normal curve*, *probability curve*, or *distribution curve* would result.

Qualitative examination of this curve reveals the following:

1. Positive and negative errors of the same magnitude are equal in occurrence.
2. Small errors are more frequent than large errors.
3. Accidental errors of great magnitude do not occur.
4. The probability of occurrence of an error is a function of its size.

Thus, it may be seen that the data derivable from the curve coincide with experience, at least qualitatively. Indeed the curve itself may be mathematically derived on the basis of these assumptions, but it is not the purpose to do so here. Actually, the equation for the curve may be expressed thus:

$$y = \frac{h}{\sqrt{\pi}} \cdot \epsilon^{-h^2x^2}$$

The value h for a given series is referred to as its *index of precision*. In the ideal case, the index of precision is related to the average deviation, thus: a.d. $= 1/(h\sqrt{\pi})$.

Founded upon the normal distribution law is the *theory of least squares* which states that the *most probable value* of a quantity obtainable from a number of measurements of equal precision is that value for which the sum of the squares of the errors is a minimum. As pointed out above, this is found to be the arithmetic mean.

The *probable error* (p.e.) is an error of such magnitude that the probability of its being less than the true error is equal to the probability of its being greater than the true error. From the equation for the normal curve, it can be shown that the probable error is related to the average deviation, thus: p.e. $= 0.8453$ (a.d.).

One interesting property of the probable error is that 50 per cent of all measurements will fall within the range M $\pm$ p.e. where p.e. is the probable error of a single measurement. The probable error also is used to determine when doubtful measurements are to be rejected. This forms the basis of the method of Pierce and Chauvenet[2] which is generally regarded as superior to the method given above. The procedure is to determine the mean and probable error of a single observation from the series of measurements, retaining the doubtful values; and then divide the deviation of the doubtful value from the mean by the probable error of a single observation. Let the absolute value of the quantity so obtained be t. A table is now consulted, in which the greatest permissible values of t are given according to the number of observations n. If the value of t for the doubtful measurement is greater than the limiting value given in the table for the corresponding number of observations, the suspected observation should be rejected.

An abridged form of the table follows:

n	t	n	t
3	2.05	11	2.96
4	2.27	12	3.02
5	2.44	13	3.07
6	2.57	14	3.12
7	2.67	15	3.2
8	2.76	20	3.3
9	2.84	50	3.8
10	2.91	100	4.2

A practical illustration of the statistical data given above is as follows:

A series of tensile strength measurements are made on the samples of a textile fabric. The values in pounds obtained are:

3, 20, 25, 18, 22, 18, 18, 24, 21, 18, 22.

Assuming equal precision, the following observations can be made:

(1) The value 3 is to be rejected.
(2) The arithmetic mean is 20.6.
(3) The most probable value is 20.6.
(4) The modal value is 18.
(5) The median value is 20.5.
(6) The average deviation is 2.2.

[1] Some authorities recommend the rejection of the value if its difference from the mean is greater than *four* times the average deviation.

[2] CHAUVENET, "Spherical and practical astronomy," Lippincott, Philadelphia, **1868**, Vol. II, p. 558.

(7) The standard deviation is 6.9.
(8) The probable error is 1.9.

Since the above treatment of measurements has been simplified to include only measurements of equal precision, it would be useful to conclude by explaining how measurements of unequal precision are dealt with. Certainly measurements made with varying degrees of precision are not infrequent. If, then, a given measurement is twice as precise and thus twice as reliable as the other measurements in the series it is reasonable to expect that more nearly true values of statistical functions such as the mean would be obtained by treating the measurement as two separate but identical measurements. In that way, the measurement would have twice the weight of any of the other measurements in its effect on statistical functions.

In general a measurement is said to have a *weight* of W if it is equivalent in importance to W measurements. By an extension of the argument given above, it may be shown that the mean of a series of measurements V_1, V_2, $V_3 \ldots V_n$ having weights of W_1, W_2, $W_3 \ldots W_n$, respectively, is given by the formula:

$$M = \frac{V_1W_1 + V_2W_2 + V_3W_3 \ldots V_nW_n}{W_1 + W_2 + W_3 \ldots W_n}$$

Similarly, the mode may be redefined to include weighed measurements as being that value having the maximum total of weights associated with it.

PRACTICAL OBSERVATIONS

It should be apparent from the foregoing that the error of any given measurement will have less effect upon the error of the mean as the number of measurements is increased. Thus, if the error of any given measurement is increased 3 units, the error introduced in the mean will be only 0.3 unit if 10 measurements are made, and only 0.03 unit if 100 measurements are made.

In general, the greater the number of measurements, the greater is the reliability of the arithmetic mean as an approximation to the true value. Indeed, it may be shown that the arithmetic mean derived from n measurements of equal reliability is $\sqrt{n}$ times as reliable as any single measurement.

It is to be noted, also, that the methods of handling accidental errors, as outlined above, do not correct for constant errors. If there is a constant error running through a series of measurements, the arithmetic mean will also carry the same error.

In making calculations, it very often happens that the results of different kinds of measurements are combined; and since these quantities usually have different probable errors, it is often desirable to know the probable error of the final result. In conclusion, then, the following formulas are given:

1. The probable error of the sum or difference of two quantities A and B which have probable errors of $\pm a$ and $\pm b$, respectively, is

$$\text{p.e.} = \pm\sqrt{a^2 + b^2}$$

2. The probable error of the product of the two quantities A and B is

$$\text{p.e.} = \pm\sqrt{(Ab)^2 + (Ba)^2}$$

3. The probable error of the product of the quantities A, B, and C (where $\pm c$ is the probable error of C) is

$$\text{p.e.} = \pm\sqrt{(BCa)^2 + (ACb)^2 + (ABc)^2}$$

4. The probable error of the quotient B/A is

$$\text{p.e.} = \pm\sqrt{\frac{(Ba/A)^2 + b^2}{A}}$$

5. The probable error of the proportion $A/B = C/X$ is

$$\text{p.e.} = \pm\sqrt{\frac{(BCa/A)^2 + (Cb)^2 + (Bc)^2}{A}}$$

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NERVE GAS ON TAP

(*Continued from page 402.*)

safest, they stung him in his most sensitive places, which he had taken no thought of defending, and his body became an enormous corpse."

The moral of this story is, do not allow mosquitoes to pull your nerves and "gas" you into a stupor.

But, let us assume the worst, and grant that such gases, unknown to us, have been developed. The answer is again: "So what?" Civilian protection requires no more special technique nor apparatus than is specified for other types of war gases. Three flights up and you are safe, since no one can produce a light gas that will hug the ground with any greater success than anyone can produce a square that is a circle.

Again, there are folks who must worry to keep happy. Well, choose something useful to worry about. For example, are your city's quotas for war bonds, war production, blood banks, and relief funds fulfilled? Organize yourself with earnest intent and dedicate your will to the determination that we on the home front shall not fail those on the battle front.

Analytical Experiments in Spectrophotometry

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IN RECENT years, especially since the introduction of photoelectric instruments, there has been a greatly increased interest in the application of spectrophotometry to colorimetric problems. It has been estimated that more than a million curves are being determined annually in industrial laboratories, and this number is increasing rapidly.

Instructions are provided by manufacturers for specific instruments to guide the operator, in a general way, in the mechanics of operation; but thus far the author has not found exercises designed to give students experience in the more generally useful analytical applications (*5*) of spectrophotometers. Some years' experience with this problem has led to the compilation of the experiments outlined here. It should be noted that they apply primarily to spectrophotometers and not to filter photometers.

The need of authors and reviewers for some of the information provided by such experiments is evident on reading current periodicals. Many papers are being published in which the spectrophotometric curves are defective from the viewpoint of analytical chemists. Thus no mention is made of the method of measurement, the spectral band width is not given, the system of plotting is not well adapted to the purpose in mind, and the curves are poorly presented. Presumably those responsible must be careless or unaware of what is desirable.

In order to provide experience in obtaining and using spectrophotometric data, various colored solutions may be selected from those available. The preferable systems depend upon the characteristics which are to be studied, since many solutions diverge widely in colorimetric properties. For some experiments, such as that showing the effect of spectral band width, suitable transparent solids are just as satisfactory. Opaque solids, such as plastics and textiles, may be used for color analysis measurements.

APPARATUS

Any of the better spectrophotometers, either visual or photoelectric, may be used. Readings with visual instruments are increasingly unreliable below 440 or above 670 mμ because of the low sensitivity of the normal eye in these regions. If several different types of instruments are available, it is instructive to make a comparative study with them to determine the relative accuracy, time required, ease of operation, and other factors.

Since the technic of operating a spectrophotometer depends upon the instrument, instructions should be available for the one to be used.

In measuring solutions, the absorption cell should be carefully cleaned and finally rinsed with some of the solution to be measured. After filling the cell, the faces through which the light beam passes should be wiped dry and clean with absorbent tissue. If two cells are used, the second will contain the solvent only. Unless otherwise specified, 1-cm. cells are assumed.

SOLUTIONS

The following stock solutions, prepared as noted, may be used:

a. Potassium Permanganate. Use a solution of known concentration to prepare 500 ml. of one containing 50 mg. of manganese per liter.

b. Potassium Dichromate. Prepare 1000 ml. of a 0.1 *M* solution by dissolving material of known purity in water.

c. Iron. Dissolve 0.1000 g. of iron wire, of reagent quality, in a small amount of dilute hydrochloric acid. To insure oxidation of the iron, add some hydrogen peroxide and boil out the excess. Dilute the solution to 1000 ml. Appropriate dilutions may then be made from this stock solution which contains 100 mg. of iron per liter (100 P.P.M.).

STUDY OF SIGNIFICANT FACTORS

Some of the factors which may be encountered, either with spectrophotometers as instruments or with the solutions being measured, are illustrated in the exercises described herewith. The different solutions suggested will show the variety of colorimetric properties desired.

Spectrophotometric data, in the form of curves, may be presented in several ways, the one used depending upon the instrumental readings and the purpose for which the data are obtained. It is assumed here that the readings will be transmittancy (or reflectance), in per cent, and wave length, in millimicrons. Other systems can then be calculated from these (*1*, *9*).

a. Effect of Concentration. Set the spectrophotometer for a definite spectral band width, such as 10 mμ. Determine the transmission curves for a series of permanganate solutions having concentrations of 50, 35, 20, 10, 5, 2.5, 1.0, and 0.25 mg. of manganese per liter. Take the transmittancy readings at intervals of 10 mμ from 400 to 700 mμ.

Plot the curves with transmittancy as the ordinate and wave length as the abscissa, as shown in Figure 1. Taking 95 and 5 per cent transmittancy as the upper

and lower limits, respectively, for reliable measurement at the peak of the absorption band, what is the range of concentration that may be measured in a 1-cm. cell?

At least one of these curves should be plotted in each of the other forms often used. Other ordinates are extinction (= optical density = E = log 1/transmittancy) or log E, on a linear scale, and transmittancy (= T) on a log scale; other abscissas are log wave length or frequency (= 3×10^5/wave length, in mμ), on a linear scale, and wave length, on a log scale (*1*, *6*).

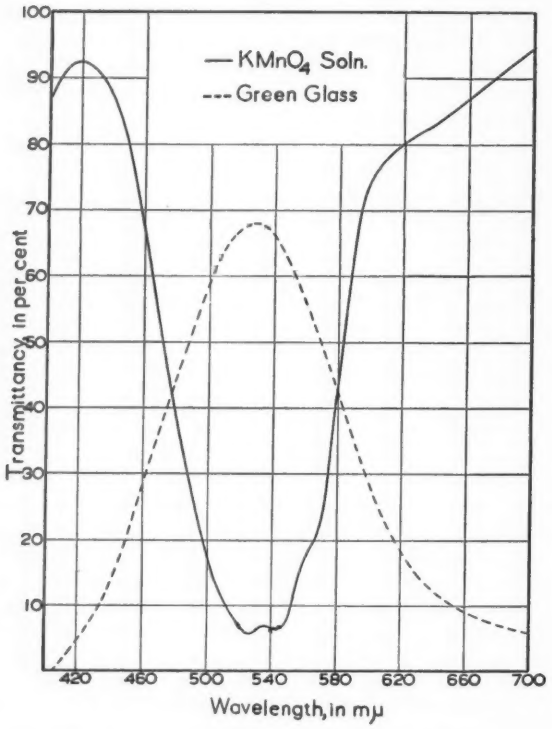

FIGURE 1.—TRANSMITTANCY-WAVE LENGTH CURVES

A curve shape index may be constructed from the curve plotted with log E as ordinate (linear scale) and log wave length as abscissa (linear scale) (*6*).

b. Effect of Cell Thickness. Using the permanganate solution containing 5 mg. of manganese per liter, determine the transmittancies in cells of different thicknesses, such as 0.5, 1.0, 2.0, 5.0, and 10.0 cm., at intervals of 10 mμ.

Plot the data in the form of a transmittancy-wave length graph to determine the optimum thickness of cell for this concentration.

c. Effect of Width of Spectral Band. Determine the transmittancies of the permanganate solution containing 10 mg. of manganese per liter for different spectral band widths, preferably 2.5, 5.0, 10.0, and 20.0 mμ, the readings being taken at intervals of 5 mμ from 480 to 580 mμ.

Plot the data on a transmittancy-wave length graph and note the difference in the curves, especially between 520 and 550 mμ.

d. Effect of Wave Length Intervals. Determine the transmittancy of the permanganate solution containing 20 mg. of manganese per liter at a spectral band width of 10 mμ (or, better, 5 mμ), the readings being taken at intervals of 10 mμ from 400 to 700 mμ.

Plot three separate, smooth curves in the form of transmittancy-wave length graphs by using the readings at intervals of 10, 20, and 40 mμ from 400 mμ upward. The effect here, as well as that for width of spectral band, is more striking for a solution of a neodymium salt or for a didymium glass. Comparison of the curve for the 10-mμ interval with that obtained on a filter photometer demonstrates one limitation of such instruments.

e. Conformity of Solution to Bouguer's Law. From the curves showing the effect of cell thickness tabulate the transmittancies for some given wave length. Preferably this wave length should be at a point of minimum transmission in the absorption band, which in the case of potassium permanganate is between 520 and 550 mμ; otherwise select a wave length where the transmittancy differences between different concentrations are large.

Using the transmittancy for some given cell thickness as a basis for calculation, such as that for 2 cm., calculate the transmittancy for the other measured thicknesses by means of the relationship:

$$T^{1/t} = T_1^{1/t_1}$$

in which T is the transmittancy of the measured solution at a given wave length, t is its thickness, and t_1 is the thickness of the solution whose transmittancy T_1 is desired. Compare the calculated and observed transmittancies. The calculated values may be checked by means of a Keuffel and Esser color slide rule.

f. Conformity to Beer's Law. From the curves showing the effect of concentration of permanganate, and for the wave length used in Section "*e*," tabulate the transmittancies for the several concentrations. Construct a curve with concentration as the abscissa and $\log_{10} T$ as the ordinate, using linear scale paper; or on semilogarithmic paper plot T directly as the ordinate and concentration as the abscissa on a linear scale. A straight line indicates conformity to Beer's law. If preferred, the extinction (optical density), as given directly on some instruments, may be plotted against concentration, using linear scales.

If conformity to Beer's law is found, calculate the molecular extinction coefficient ϵ for several concentrations by using the relationship:

$$\epsilon = \frac{\log (1/T)}{tc}$$

in which T is the transmittancy for the wave length used in Section "*e*," t the thickness, and c the concentration of the solute in mols per liter.

The exercise should be repeated with a solution such as potassium dichromate in water. Transmittancies should be determined for concentrations from 0.1 *M* down to the limit of utility. The smaller concentrations are obtained by diluting the stock solution with water.

g. Determination of the Amount of a Constituent. If transmittancy-wave length curves have been plotted for a series of concentrations of permanganate solutions, the data are at hand for determining manganese in steel spectrophotometrically. The solution of the unknown should be prepared according to directions in some textbook (*4*).

Measure the transmittancy of the unknown solution with the spectrophotometer set to pass a 10-mμ spectral band whose median wave length is one of the preferable values selected in Section "*e*." Two methods of calculating the concentration of the unknown may be tried.

In the first method a transmittancy-concentration curve is constructed from the data presented in Section "*a*" by plotting the concentrations as abscissas and transmittancies, at the wave length used for measuring the unknown, as ordinates. Then locate the measured transmittancy of the unknown on this curve and drop a perpendicular from this point to the base line to find the desired concentration.

In the second method one solves for the unknown concentration c, in mols per liter, in the expression:

$$c = \frac{\log (1/T)}{\epsilon\, t}$$

T being the measured transmittancy, ϵ the molecular extinction coefficient determined in Section "*f*," and t the cell thickness. This method presupposes conformity of the solution to Beer's law.

h. Determination of Color Analysis Constants. For the system selected for measurement determine the transmittancy, if a transparent medium, or the reflection, if an opaque medium, at intervals of 10 mμ from 400 to 700 mμ and plot the transmittancy (or reflectance)-wave length curve.

Follow the directions given by Hardy (*3*) in calculating the trichromatic coefficients from this curve. Either the weighted or selected ordinate method may be used. The procedure is simplified if a calculator is available (*7*). Having determined the trichromatic coefficients, the brightness, dominant wave length, and colorimetric purity may then be obtained.

i. Effect of Solution Variables. A number of factors affect the color of various solutions, either during production of the color or following its development. Spectrophotometric curves provide an excellent means for measuring and studying these effects. An automatic recording instrument is particularly desirable if the system undergoes rapid change.

Space is not available to provide detailed experiments under all the sub-headings. Where details are not given, the outline indicates the factor, a solution that will illustrate it, and a reference where details may be found.

a'. Sensitivity of Color-Forming Reagents. Pipet 10-ml. portions of a solution containing 25 mg. of iron per liter into a series of 100-ml. volumetric flasks. Develop colors by means of the reagents listed in Table 1, under conditions specified therein, and determine the spectral transmission curves. From the observed transmittancies, at the indicated wave lengths of maximum absorption, calculate the concentrations, in mg. per liter (P.P.M.), which would give a 50 per cent transmittancy at these wave lengths. Arrange the reagents in the order of decreasing sensitivity.

b'. Effect of Excess Color-Forming Reagent. Redetermine the curves suggested in Section "*a*'" for iron plus ammonium thiocyanate, ferron, and 1,10-phenanthroline, using the conditions specified in Table 1. Then repeat the determinations with two and with four times the amount of reagent used at first. Plot the curves as a transmittancy-wave length graph.

c'. Effect of Time on Development of Color. To 5 ml. of a solution containing 0.1 mg. of potassium dihydrogen phosphate per ml. add 5 ml. of 5 per cent ammonium molybdate solution (in 5 *N* sulfuric acid). To this add 1 ml. of 2 per cent hydroquinone and 1 ml. of 20 per cent sodium sulfite and make up to 100 ml. Determine the transmittancy at various time intervals over a period of 48 hours. Plot the curves as before.

d'. Effect of Temperature on Development of Color. To determine the effect of the initial temperature on the rate of development of the color the experiment in the previous section may be repeated. Prepare in the same way three different solutions by using reagents previously brought to 25, 50, and 75°C. Determine the transmittancies as quickly as possible. Keep the stock solutions so prepared at the respective temperatures and at the end of an hour determine the transmittancies again.

e'. Effect of pH on Color. The effect of pH may be

TABLE 1. REAGENTS FOR IRON

Compound	*Concentration, Per Cent*	*Volume, Ml.*	*Acidity Adjustment*	*pH*	*Maximum Absorption, Mμ*	*Reference: Anal. Ed., Ind. Eng. Chem.*
Ammonium thiocyanate*	20	2	HNO_3, 5 ml., 6 *M*	0.1–1.2	470	13, 551 (1941)
Ferron	0.04	10	$NaC_2H_3O_2$, HCl	2.8–3.2	440	9, 406 (1937)
Sodium salicylate	10	1	NH_4OH and CH_3COOH	2.6–2.8	520	10, 136 (1938)
Salicylaldoxime	0.1	10	1 g. $NH_4C_2H_3O_2$	6.5–7.5	490	12, 448 (1940)
Mercaptoacetic acid	10	2	NH_4OH, 10 ml., 3 *M*	10	535	10, 7 (1938)
Kojic acid	0.1	10	$NH_4C_2H_3O_2$, 10 ml., 1 *M*	5.5–6.5	440	13, 612 (1941)
1,10-Phenanthroline†	0.1	5	...	2–9	508	10, 60 (1938)
2,2'-Bipyridyl†	0.5	5	...	3–9	522	14, 364 (1942)

* Add 60 ml. of acetone before the reagent.
† Reduce the iron with 1 ml. of 10 per cent hydroxylamine.

studied most easily with a solution such as potassium dichromate, in which there is a simple equilibrium involved as represented by the equation:

$$2CrO_4^{--} + 2H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$

Prepare two series of solutions of potassium dichromate, one $M/250$ and one $M/1000$, ranging in pH from 3 to 9 in units. As solvent use standard buffer solutions and adjust the pH finally with dilute sulfuric acid or potassium hydroxide. Determine the transmittancies and plot the curves in the usual manner.

Strikingly different effects may be obtained with solutions of iron and the color-forming reagents listed in Table 1. For this purpose use ferron, salicylaldoxime, and 1,10-phenanthroline. After the reactants are mixed and diluted nearly to 100 ml., add dilute hydrochloric acid or sodium hydroxide to adjust the pH to the desired value (determined preferably with a glass electrode), and then bring the volume to 100 ml. Determine the curves, at intervals of about 1 pH unit, from 1 to 5 for ferron, and 3 to 9 for salicylaldoxime and for 1,10-phenanthroline.

Interest may be added by determining the family of curves showing the hues of an acid-base indicator at pH values through its transformation range (*2*). Universal indicators show a greater range of hues (*8*).

f'. Stability of Color. Use the iron solution and ammonium thiocyanate specified in Table 1. Omit the acetone and use hydrochloric acid to bring the pH in the range 1.5 to 2.5. Determine the curve immediately and at intervals of several hours.

g'. Effect of Solvent. To 10 ml. of a solution containing 0.04 mg. of iron per ml. add 5 ml. of 6 *M* nitric acid, 2 ml. of 20 per cent ammonium thiocyanate, dilute to 100 ml., and determine the transmission curve.

Repeat this determination using enough acetone for dilution in order to make its concentration 20, 40, 60, and 80 per cent by volume.

h'. Effect of Diverse Ions. In many cases the presence of ions other than the one to be determined colorimetrically interferes more or less seriously with the color. The magnitude of the effect may be calculated from the relationship:

$$T_1 = T_2^{C_1/C_2}$$

T_1 and C_1 and T_2 and C_2 being, respectively, the transmittancies, at a given wave length, and the concentrations of the unknown and the standard solutions.

In the references cited in Table 1, or in the sections mentioned, examples of the following types of interference may be found:

a". Increase in Color. Both the interfering ion and the ion to be determined form similarly colored systems with the reagent (arsenate and silicate ions in the molybdenum blue method for phosphorus—see section "*c'"*).

b". Decrease in Color. The interfering ion forms a colorless complex with the color-forming reagent whose effective concentration is thus reduced (ferric ion + aluminum ion + ferron); the interfering ion reacts with the ion to be determined by forming a colorless complex (ferric ion + pyrophosphate ion + ferron), or by rendering the ion to be determined inactive through oxidation or reduction (ferric ion + chlorostannous ion + thiocyanate ion); the interfering ion forms a precipitate which reduces the transmittancy (ferric ion + tungstate ion + thiocyanate ion).

c". Change of Hue. The interfering ion and the reagent form a colored complex having a hue different from that formed with the desired constituent (ferric ion + molybdate ion + salicylaldoxime); the interfering ion is itself colored (ferric ion + cobaltous ion + thiocyanate ion).

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THE PREPARATION OF AMMONIUM HYDROXIDE FOR LABORATORY USE

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KOBE AND MARKOV[1] have described a process for the preparation of ammonium hydroxide for laboratory use in which ammonia gas is bubbled through water. Due to the exothermic nature of the reaction the solution becomes heated above room temperature and the resulting decreased solubility necessitates a series of absorption bottles to prevent the loss of ammonia to the air. In this paper a simpler apparatus is described in which cooling arrangement shortens the time of preparation and avoids the use of a series of absorption bottles.

[1] KOBE AND MARKOV, J. CHEM. EDUC., **18,** 29 (1941).

APPARATUS

A tank of liquid ammonia is connected by rubber

tubing to a 40-liter carboy containing 25 liters of water. The 12-mm. glass tubing through which the ammonia is passed into the water is curved to somewhat conform with the curvature of the carboy, Figure 1. The end of the tube is about one inch from the bottom and one inch from the side of the carboy. The exit tube from the carboy is led into a tall hydrometer jar filled with water to which 5–10 drops of phenolphthalein have been added.

The cooling device is a hollow iron ring, such as a circular gas burner, which has numerous small holes around its circumference. The ring is placed over the neck of the carboy and cold tap water run through it so the water sprays evenly over the shoulders of the carboy. A few towels are wrapped around the carboy to further increase the cooling efficiency.

PREPARATION

The apparatus is arranged as shown in Figure 1. The carboy is set in a sink or near a drain and tap water run through the cooling ring continuously. The valve on the ammonia tank is opened wide or just less than to where "bumping" in the carboy is objectionable. If the ammonia valve is left open continuously for many hours a layer of frost collects on the outside of the tank, thus reducing the rate of flow of gas. In such case the rate may be increased again by warming the tank with water. The authors usually found it more convenient to operate the absorption for only three or four hours at a time, thus avoiding excessive cooling of the tank.

After about 16 hours of operation the volume of solution in the carboy has increased from 25 to approximately 40 liters. At about this time enough ammonia has passed into the hydrometer jar or tall cylinder, under a head of about 12 inches of water, to turn the phenolphthalein pink. The ammonia gas is then shut off and the specific gravity of the solution in the carboy is measured. A portion may be removed from the carboy, warmed to room temperature, and tested with a hydrometer. By rearranging the connections on the carboy the pressure from the ammonia cylinder may be used to start a siphon action.

If the hydroxide does not give the specific gravity usually desired, 0.9, the absorption is continued. During the final stages, the rate of flow of ammonia is reduced to minimize the loss of the gas from the carboy.

As a safety measure a water trap may be inserted between the tank and the carboy to prevent water from sucking back into the tank. However the authors prefer to partially close the tank valve and pull off the rubber tubing at the tank simultaneously with shutting the valve on the nozzle.

DISCUSSION

The mixing of the solution in the carboy is well done by the ammonia being led into the water in a horizontal direction near the edge of the carboy. The rising of the undissolved ammonia further aids the mixing.

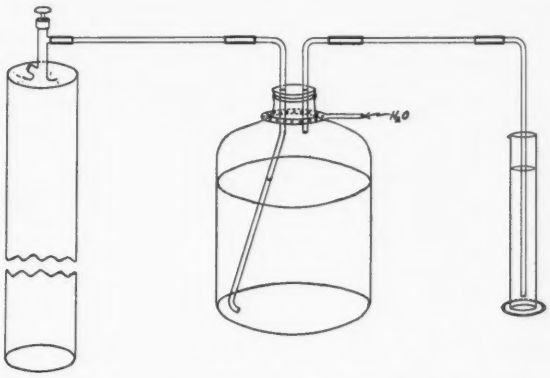

FIGURE 1.—APPARATUS FOR THE PREPARATION OF AMMONIUM HYDROXIDE

The cooling ring, the most unique part of the preparation, was an old burner designed for a small still. Similar burners may be obtained from any chemical supply house at a nominal cost.

During one preparation the hydrometer jar was replaced by a four-liter flask of water. About 40 liters of solution, specific gravity 0.9, were prepared by passing ammonia for 17–18 hours. The ammonia dissolved in the flask was found by titration to be 17.6 g. This value represented a loss of 0.17 per cent of the 10,680 g. of ammonia dissolved in the carboy. The cooling tap water was 12°C.

Some laboratories prepare ammonium hydroxide from ammonia in the winter months and store some for summer when it is impossible for them to prepare it by their present methods. Using the arrangement described in this paper such laboratories could release many carboys. A national shortage of carboys has recently been reported.

CORRECTION

FORMULA OF THE MONTH

We discovered last month, too late, that the formula for propylene glycol had been incorrectly printed, as trimethylene glycol. Several lynx-eyed readers made the discovery as quickly as we did. The correct formula: $CH_3{\cdot}CHOH{\cdot}CH_2OH$, instead of $CH_2OH{\cdot}CH_2{\cdot}CH_2OH$. If only the hydroxyl radical would change place so easily!

Reclaimed Rubber

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WHEN the secret of vulcanization was discovered, the world was given a new material with which to work. Rubber, of course, had been used in many ways by the white man after Columbus made his first voyage of discovery and by the Indians long before that. The year 1839, however, marked the beginning of a new era. It was in this year that Charles Goodyear discovered that when sulfur and rubber are intimately mixed and heated, a product much more useful than the original rubber is obtained. Credit must be given also to Nathaniel Hayward who, prior to this, developed solar vulcanization, a process never completely successful, and to Thomas Hancock, who, working independently in England, also discovered the value of vulcanized rubber.

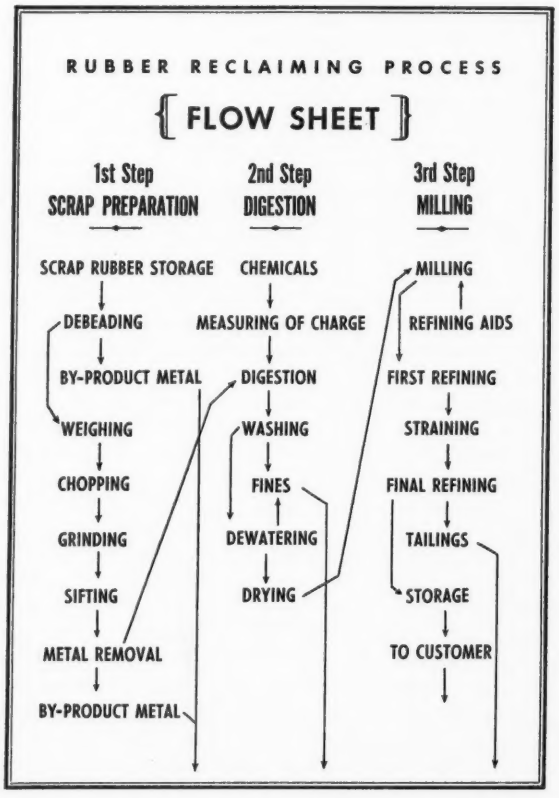
The patents covering this work were not issued until 1844; but it was in this period that "gum elastic" assumed an importance not immediately apparent, yet nevertheless epochal in its effect upon the ensuing industrial revolution. Without vulcanized rubber who can say how far the mechanical genius of our late 19th and early 20th century experimenters would have carried us? A moment's analysis will show that it is basic in the development of transportation, communication, and mechanization.

Finding the answer to the way in which rubber might be used successfully, however, solved one problem and created a new one. Rubber once vulcanized was found to be no longer amenable to normal processing operations, and no methods were known by which its original properties could be restored.

Goodyear, Hancock, and a great many others began to wonder what should be done with the scrap rubber which began to accumulate. Rubber in this period was not plentiful, and a use for the vulcanized scrap from worn-out and discarded rubber articles was diligently sought.

Previously, unvulcanized scraps had been dissolved in various solvents or simply reworked in the mixers or on the mills of those times. Now it was found that "cured" rubber no longer responded to this treatment. We quote from Goodyear's book, "Gum Elastic," published in 1855:

> "Its power of resistance to the solvents and all other destructive chemical agents is truly great. The most delicate of the fabrics made of this material may be brought in contact or immersed with impunity in such chemical liquids as sulphuric or nitric acids, sulphuric ether, oil of turpentine or any of the essential oils. Or they may be boiled in potash, lime, chloride of lime, soap suds, etc., by which ordeal, so far from being injured, they are rather improved."



Nevertheless, Goodyear and his English contemporary, Hancock, were both granted patents for the reclaiming of rubber. The former simply ground the scrap and used it as a filler, while the latter described a process of boiling scrap shreds in turpentine.

The task of recovering rubber from scrap was complicated a century ago, as it is now, by the fact that the great majority of rubber items used contained fabric of some description. The problem was really not only to plasticize or dissolve the rubber, but also to destroy or disintegrate the cotton or woolen fabric present. Beer, another early experimenter, was issued a patent in 1855. He boiled rubber scrap in lye to remove the free sulfur[1] and destroy the fabric.

[1] Free sulfur is a term used by the rubber technologist to describe that portion of the sulfur originally mixed with the rubber which does not combine with it chemically when the mixture is heated. There is usually some such sulfur present after vulcanization.

Although this method partly anticipated the present-day alkali process, the heat applied was not great enough to depolymerize the rubber hydrocarbon chain. This change seems to be the most logical explanation of the plasticization accomplished in modern reclaiming. Beer's treated scrap remained hard and unworkable.

Combined sulfur was not removed by Beer's process and has not been removed by any other commercially feasible method developed down to the present day. The formation of the rubber-sulfur vulcanizate remains in the class of irreversible chemical reactions. To use a homely illustration, the difficulties involved are about the same as those which would be experienced in trying to unscramble an egg.

Other reclaimers of this period included Hiram L. Hall, who used live steam and tar rather unsuccessfully, and C. H. and D. E. Hayward, who attempted to use sulfuric acid.

In 1871 E. H. Clapp evolved a process for separating rubber from fiber by means of an air blast and then later treating the rubber with steam. This made a very inferior product, however, since the recovered rubber was never free of fabric, and the removed fabric still contained much rubber. Furthermore, the resulting product was still not very workable.

Somewhere during this early development period of the reclaimer's art, the name "shoddy" was used for the product, a term which has stuck almost to the present day. There are still a few old-timers in the industry who use the term; most modern rubber compounders, however, refer to the material simply as "reclaim" or "reclaimed rubber."

The first workable process for reclaiming rubber was developed by a Philadelphian, Colonel Chapman Mitchell. A patent covering this process was granted in 1881. Colonel Mitchell used dilute sulfuric acid to destroy the fabric in the ground rubber scrap by boiling it for several hours in lead-lined wooden tanks. The defibered rubber was then washed free of sulfuric acid and heated in closed vessels at about 300°F. for 24 hours.

Here for the first time we find a successful reclaiming process at a temperature above that obtained by steam at atmospheric pressure or by boiling in water. This procedure softened the rubber to the point where it became again a truly plastic material similar to the original crude rubber.

The process, although useful at the time, has been gradually discarded until today reclaim made by the acid process finds application in only a very few products.

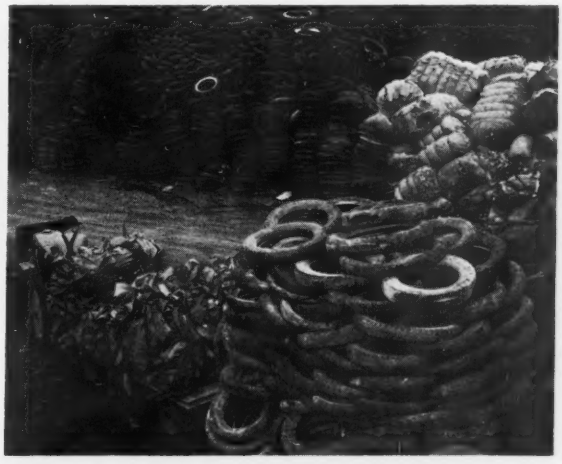
The turn of the century marked the beginning of the present reclaiming industry for it was in that year, 1899, that a brilliant young chemist was granted a patent for a method of reclaiming rubber by what has become known as the "alkali process." The basic principle established by the work of this experimenter, Arthur Marks, remains to date the best known method for reclaiming vulcanized rubber.

Marks did not discover anything essentially unique. It had long been known that alkali solutions destroyed cotton and woolen fabrics. It had also been known that rubber was softened by heat. It took Marks's ingenuity, however, to combine these known factors into a practical method.

The first effort was, of course, extremely crude. The rubber scrap containing fiber was ground and then heated in a closed vessel with a diluted caustic soda solution for 20 hours at 360°F. The cellulose hydrolyzed and could be washed free of the rubber after the digestion. Free sulfur present was partly combined with the rubber by the heat and partly removed by the action of the caustic especially from the surface of the rubber particles. These softened and defibered particles could be milled and reused in a number of items, and the process was very soon successfully exploited.

The role which caustic plays in the reclaiming process has never been fully explained. It is known that reclaim produced by the acid process or by simply a "water cook" does not possess, when revulcanized, the same physical properties as reclaim produced by the alkali method. Tensile strength and elongation are much higher for the alkali reclaims. In addition to this, the working properties, which are so important in the fabrication of finished rubber goods, are much different. Alkali reclaims are softer and have more "nerve." The acid reclaims are "flat milling," and are generally characterized by a distinctive dryness or harshness.

Up to the present time no reclaiming process has been evolved which, from a theoretical standpoint, does more than Marks's did. The modern reclaim and the plant which produces it, however, no more resemble the crude material and the glorified cooking pots of Marks's time than the modern streamlined automobile resembles the first "horseless carriage." Commercial reclaimed rubber today is made in highly mechanized factories containing heavy and expensive equipment. Discarded tires, inner tubes, and other usable scrap items



SCRAP RUBBER STORAGE YARD

undergo a complete metamorphosis and emerge as a useful raw material, carefully made, scientifically controlled, and remarkably uniform in quality and processing characteristics. Reclaimed rubber is acknowledged to be more uniform, in fact, than crude rubber.

Generally speaking, reclaimed rubber should no longer be considered as a substitute for crude rubber. It is rather an auxiliary material to be used in conjunction with crude rubber for producing certain desired effects.

Reclaim is not an adulterant or diluent and is not considered as such by modern compounders. In spite of this, however, its use still does become more desirable as the price of crude rubber advances or its availability decreases. The first 25 years of this century saw a gradually expanding use of reclaim as the quality of the product improved.

In the year 1925 the average price of crude rubber suddenly rose to 72 cents per pound with peak prices well over $1. This abnormally high price for crude rapidly increased the use of reclaimed rubber until in 1928 there was one pound used for every two pounds of crude. This high price for crude rubber was brought about by an effort to control the plantation output on the part of the British. Usually, when an attempt is made to control artificially the economics of supply and demand, things get out of hand. The debacle following enactment of the Stevenson Restriction Act[2] is well known and is not part of this story except in its effect upon the fluctuation in the use of the two materials in question.

Our country should have learned during past years that America needed an independent rubber supply. Retrospectively considered, it seems shameful at the present time, in spite of lessons learned fifteen years ago (twice the time it takes to bring a rubber tree into bearing), that this hemisphere still produces only 2 per cent of the world's rubber supply!

By 1932 crude rubber got down to a low price of less than 3 cents per pound. High grades of reclaim even during depression times could not be produced and sold at such a figure. First-grade tire reclaim sold at 5 cents in 1932, and the ratio of usage dropped until a point was reached where only 16 per cent of all the rubber used was reclaimed rubber. As we climbed out of the depression, the price of rubber increased, as did the use of reclaim until just prior to Pearl Harbor the ratio of reclaim, to crude rubber used was again about 1:2.

As the visitor approaches the modern rubber-reclaiming plant, he will probably be impressed with its size. The material can be produced in small quantities, but it

[2] The Stevenson Restriction Scheme (1922–28) tried to raise the price of crude rubber from British-owned territory by restricting production and imposing high export taxes.

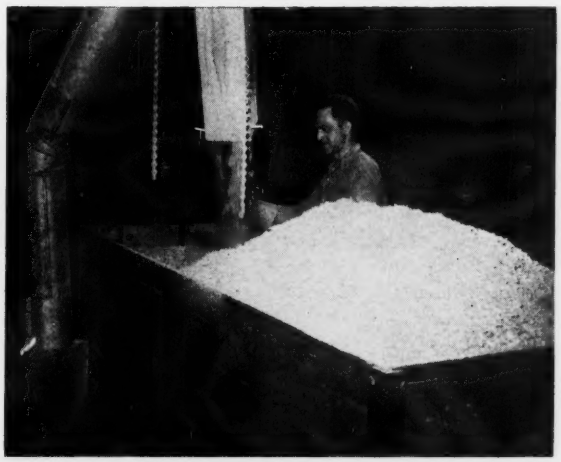
CHOPPING THE CHARGE OF SCRAP (FIRST STEP)

is only by continuous operation and in large volume that it normally can be made and sold on a profitable basis. The conversion of scrap to useful raw material is truly a "mass production" job.

Hence, the mechanical engineer working with the chemist and rubber compounder has assembled an enormous amount of equipment and has tied it together into a beautifully synchronized whole. First of all, one will find "straight line" type of production. Scrap, chemicals, and pigments enter the plant at one end and are conveyed in a straight line, sometimes by conveyer, at other times by blowers, and again simply by gravity flow, to the warehouse at the opposite end where the finished product is loaded into cars and trucks for shipment.

A better understanding of the steps involved can be obtained by first referring to the flow sheet. It will be noticed at once that the process falls logically into three major divisions. The scrap rubber must be prepared for the treatment in the pressure vessels. This scrap preparation is the first step. The second step of the process, in addition to the autoclave treatment just mentioned, includes the washing and drying of the treated rubber. The third step is a milling operation. Here the rubber is refined and formed into slabs.

The great bulk of the rubber scrap of this country used by the reclaiming industry is in the form of discarded tire casings and inner tubes. There are a number of reasons for this:



SCRAP AFTER THE DRYING OPERATION

1. *Uniformity.* The composition of tires and tubes and the method of producing them is very much the same for all manufacturers. This makes this class of scrap dependable for the production of reclaimed rubber of uniform quality.
2. *Availability of scrap.* Since the automobile is universally used, this type of scrap occurs in large volume in all settled sections of the country.
3. *Price stabilization.* Since scrap is all of one class, a stable market exists in normal times. This, of course, has a beneficial effect on selling price of reclaim.
4. *Ease of handling.* The form of the scrap makes it possible to design machines for ease of receiving, storing, and processing.
5. *Good rubber content.* There is no class of rubber product which yields such a high rubber content on a volume basis.

This does not mean that other types of scrap are not reclaimable. As a matter of fact, in the present rubber emergency it is probable that all of the rubber scrap of the country will have to be accumulated and reclaimed. As this article is being written there is much talk of a "Victory" grade of reclaim to be made from the miscellaneous collection of scrap which the government-sponsored drive will bring in through local filling stations.

STORAGE BINS FOR GROUND SCRAP (SECOND STEP)

Some reclaimers have for years been producing for specific purposes grades of reclaims other than tire and tube. These are usually called "Blends." For instance, reclaim made from boots and shoes is used in rubber proofing, and low-cost grades have been used in auto mats and stair treads.

As stated above, the reclaimer usually starts with tires or tubes. The tires are almost always debeaded by the scrap seller although in some cases the debeading is done by the reclaimer himself. In either case, this operation consists of placing each tire in a machine which quickly cuts out the bead by means of revolving circular knives. The bead is that part of the tire which fits snugly on the rim of your automobile wheel. It consists of braided steel wire built up into the form of a core, each wire being well insulated with rubber and the whole covered with rubber-impregnated fabric. The rubber in this bead can be largely recovered and reclaimed, but the cost in normal times is high; therefore, in the past beads have been largely discarded. The wire used is of good quality steel, and much of this is now being recovered along with the rubber.

In the case of inner tubes the brass valves are removed and the metal reclaimed. Metal of any kind left in the scrap would injure the grinding and sizing machinery used in the process. After the removal of the

metal each charge of scrap is carefully weighed and is run on a batch basis through the entire process.

The batch of scrap is next chopped and ground. There are several methods of accomplishing this, but the usual way is to feed the rubber into a chopper. This machine is like a gigantic lawn mower set upside down. The blades revolve, and the scrap rubber is chopped into pieces. The machine is heavy enough to handle a large truck tire which will be reduced to sliced pieces from a half inch to an inch in width in a very few seconds.

These "slices" are then ground on corrugated roll mills. These "crackers," as they are called, consist of two heavy spirally corrugated steel rolls. They are usually 32 inches long and from 21 to 24 inches in diameter. The rolls are set close together and revolve toward each other at unequal speeds. The rubber pieces dropping onto the "bite" of one of these mills are torn and ground into smaller pieces.

THE MILL ROOM (THIRD STEP)

A battery of sizing screens over which the ground scrap is passed retains the larger pieces. These are then conveyed back to the crackers for reworking, and the material which is fine enough to pass through the specified screen mesh goes into the waiting storage bin. On the way to the bin the finely ground scrap passes through a magnetic separator which removes all ferrous metal. This operation is quite important to the final quality of the product as metallic contamination is extremely undesirable. This metal removed consists of whatever bead wire might be left over from the debeading and any iron or steel particles picked up by the tire during service. At the end of a shift there has usually been collected at this point quite a quantity of potential or actual "punctures."

This brings us to a description of the second step in the process—"Digestion."

The charge of rubber is now in a batch storage bin directly over the digester. These vessels are technically simple autoclaves. They are internally agitated either horizontally or vertically, are steam jacketed, and the outer shell is heavily insulated with asbestos lagging. Usually they hold a 4000 to 6000 pound charge of rubber scrap and approximately 1000 gallons of 4 to 6 per cent caustic soda solution. In addition to this, oils and softeners of various kinds are added in different percentages depending on the grade or type of reclaim being manufactured. Materials used are pine tar, coal-tar derivatives, asphaltic products, various resins, rosin, and many others. These softeners help swell and soften the rubber particles under the digesting conditions much more than they would if simply added during milling or refining as described in the third stage.

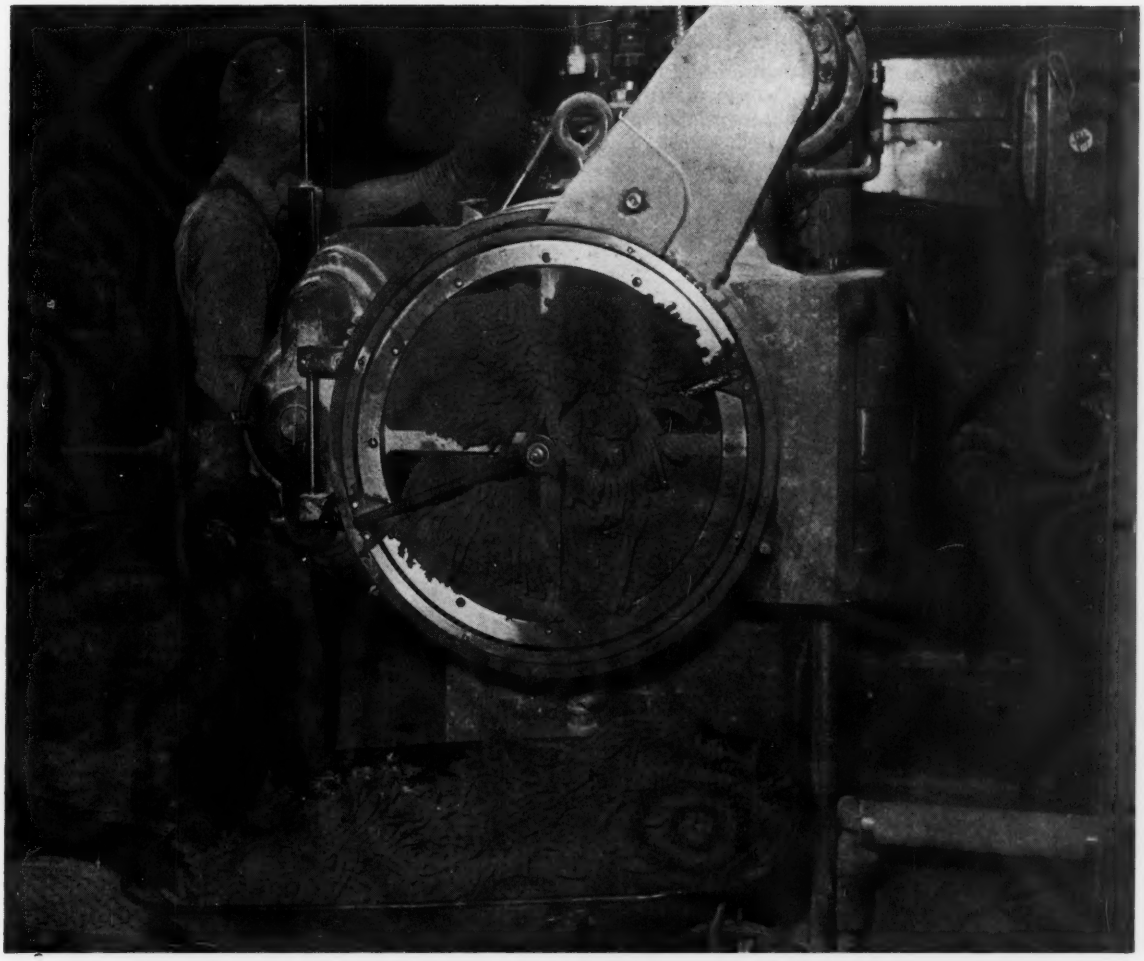
The sequence of operations is as follows: the chemicals needed are carefully weighed or measured, the calculations being based on the weight of the scrap rubber. The caustic soda solution is made up and scrap rubber, chemicals, and the caustic solution are charged into the autoclave. The agitating mechanism is then started, and the machine is sealed. Steam is turned into the jacket. This gradually raises the internal pressure, and the digestion is under way. The period of the treatment is from 10 to 20 hours depending upon the steam pressure in the jacket which may be controlled at from 150 to 200 pounds per square inch. An internal pressure is developed in the vessel about equal to the steam pressure in the jacket.

At the end of the period the charge is a soupy mass which can be handled through special types of pumps or by gravity flow. This digestion is the heart of the process, and it is here that Marks's principle is applied.

Tire scrap when charged into the machine consists of ground rubber intimately mixed with cotton which was originally the tire cord. Later when this is discharged from the autoclaves into a washer magazine, it has lost all of its fiber. The action of the caustic soda at the elevated temperature and pressure of the digestion has partly decomposed and hydrolyzed the cellulose; it exists then as sodium carbonate in the digester liquor and as other soluble cellulose derivatives. In addition to having lost its fiber the rubber is now soft and plastic. By the time it is washed and dried, it is in most cases actually sticky.

The washers are of many types. All have one purpose, however, to wash the rubber free of the liquid which was with it in the digester. This liquor is usually dark brown in color and quite complicated in composition. It contains some excess of alkali, reaction products formed by the various chemicals added, and the cellulose by-products. The presence of sulfur (from the free sulfur in the rubber scrap) further complicates the composition until this liquor is truly a veritable nightmare of organic chemistry.

The action of the washer leaves the rubber clean. All of the digester liquor is removed; and although there does remain some residual alkali, the amount is usually less than 0.1 per cent calculated as NaOH. From the washer flows a mixture of the digester liquor greatly diluted by the wash water and a fine sludge-like material consisting of partly hydrolyzed cellulose, fine particles of rubber, and other impurities. This mixture is settled in large tanks, and the clear liquor on the top



THE STRAINING OPERATION (THIRD STEP)

is decanted and discarded. After further concentration it is filtered to reduce moisture content, and the cake dried by means of hot air. This dried material which has a very low rubber content is used chiefly as a filler in low-cost reclaims.

The final operation in step 2 is drying. This is usually done by mechanical driers employing a forced draft of hot air blown through a thin layer of rubber. Finally the rubber is collected in tractor cars for ease of handling. Approximately 6 per cent of water is retained. This keeps the material cool by evaporation during subsequent milling operations.

Before leaving the "Digestion Step," it is important that mention be made of the "pan process." In this method of reclaiming, scrap rubber is mixed with various chemicals and dumped into pans. These pans are then loaded into a single shell pressure vessel and the door sealed. Live steam is turned into the vessel, and after a number of hours at approximately 150 pounds of steam pressure the material is taken out and is ready for the milling step. The "pan process" is applicable only to fiber-free stock since the cellulose is thereby not destroyed and cannot be removed effectively. Reclaim of good quality can be manufactured by this process, but the digester treatment is considered more efficient.

The final step in the process of reclaiming is described briefly on the flow sheet as "milling." This step is extremely important. It is the mill room which is the most costly part of the modern reclaiming plant. The rubber is now defibered, softened, washed clean, and dried. The mass consists, however, of small pieces about the size of lead pencil erasers. These pieces are soft and sticky. They are put on a rubber mill so that they will cohere into a sheet or blanket necessary for subsequent refining. This mass is extremely granular and lumpy. Many phases in the processing of rubber require a smooth, free-flowing plastic mass. This is particularly true where an extrusion or calendering operation is involved. The problem then is to furnish

the rubber goods manufacturer with a product which is free of lumps and uniformly smooth and workable.

The equipment to do this work is a series of mills or Banbury mixers, refiners, and strainers. Orthodox

RUBBER MIXING OR MASSING MILL (THIRD STEP)

rubber mills are usually preferred to Banburys. This type of machine consists of two smooth steel rolls from 60 to 84 inches in length and from 20 to 28 inches in diameter. The two rolls are usually slightly different in diameter and revolve toward each other at slightly different peripheral speeds. These are for mixing or massing the dried rubber.

The refiners are of shorter roll length and are built heavier. Otherwise, they are very much the same in

FINISHED SLAB OF RECLAIM (THIRD STEP)

appearance as the mills. These are the machines which crush the lumps and form the rubber into smooth sheets.

The strainers are like huge meat grinders. The rubber is fed into a hopper where it is picked up by an endless screw and forced against and through a fine mesh screen. These machines are heavy and powerful, and their function is to remove any extraneous matter present in the rubber. All of the machines in this step are water cooled to remove the heat developed by working the rubber.

Referring back to our flow sheet to get the proper sequence of operations, the dried stock is delivered to the mills by trucks or conveyors. Here is added any compounding material necessary to aid in the refining. Pigments of various kinds are used, some for the refining and some to give certain desired or specified characteristics to the finished reclaim. Also, uniformity is controlled here by adjusting pigment so that a constant specific gravity of the material is maintained.

The rubber is fed to the bite of the mill and the pigment worked in by the action of the rolls. When the

FINISHED RECLAIM IN STORAGE WAREHOUSE

material has been massed, an operation which takes five or six minutes, it is taken off the mill and put through the first refining. The rolls on these machines are set so that the massed rubber squeezes through and comes out as a sheet approximately 0.015 inch thick.

After this first refining the material is put through the strainer previously described. The strainer screen is approximately 20 mesh. It is surprising how much foreign matter is removed here.

The strained rubber is then given the last step in the process—final refining. This step is just like the first refining only that the refiner rolls are set much closer.

These refiner rolls are ground on precision machines so that the roll will be deflected by the pressure of the stock being squeezed through just enough to produce a sheet of rubber uniform in thickness from one edge to the other. Careful control of the cooling water is also a factor in the proper operation of these rolls.

The sheet of a well-refined, high-grade reclaim coming off the finishing refiners is approximately 0.003 to 0.005

inch thick. This tissue thin sheet is taken up by a revolving drum attached to each machine, and a slab is gradually built up layer after layer until it is approximately an inch thick. It is then quickly cut off with a "zip" of a rubber knife, and our slab of reclaim weighing about 30 pounds is ready for the shipping room.

Reclaim is used today in all but a very few of the familiar articles of rubber with which all of us come in daily contact. War in the Far East has increased this use, and the rubber technologists of America are finding in this emergency ways to use reclaim that were undreamed of six months ago. We have an industry capacity in this country of some 350,000 tons annually and enough scrap to go ahead for several years at least.

By that time we will have synthetic rubber, and work already carried out at the Massachusetts Institute of Technology has solved the problem of reclaiming this material. We shall be ready for it, therefore, when it begins to come back as scrap to the reclaiming companies.

As this article is being written more than 90 per cent of the rubber-producing territory of the world is in enemy hands. The little island of Ceylon off the tip of India still is in the hands of the allied nations; it is the last important rubber-producing center to which we have access. Ceylon produces between 6 and 7 per cent of the world's rubber. Whether or not we are still obtaining shipments from this island is not known. We do know, however, that if civilian consumption is drastically curtailed and wise use made of our present stock pile, reclaim rubber can bridge the gap.

America will get by in spite of its most critical raw material shortage due to the evolution of an idea that Arthur Marks had back in the 1890's.

A Low Temperature Vacuum Drying Apparatus

D. H. COOK

School of Tropical Medicine, San Juan, Puerto Rico

THE USE of dried plasma has stimulated the development of apparatus for drying frozen materials or the evaporation of water from unstable solutions at a low temperature. In 1939 Greaves and Adair (*1*) made a critical study of the drying of solutions of proteins from the frozen state and designed efficient but elaborate apparatus for this purpose.

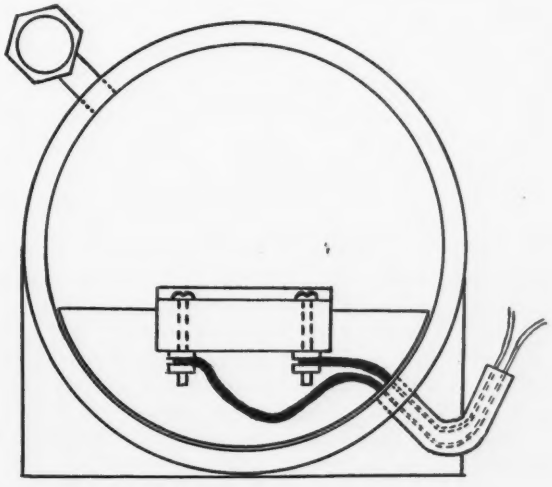
Previously Stevens (*2*) had developed a relatively simple apparatus for drying protein solutions at low temperatures but under the present conditions even his equipment would be difficult to obtain.

Having the problem of concentrating small volumes of enzyme solutions we have constructed an apparatus from parts available to almost all laboratories; an apparatus that can handle 100–150 cc. at a time and remove that volume of water in 24 hours.

A piece of four-inch internal diameter galvanized pipe, six or eight inches long which fitted snugly into the lower tray compartment of an electric refrigerator was found in the junk pile. A piece of galvanized sheet iron 16 gage was soldered to one end giving a vacuum tight seal, and the sheet iron was cut to a semicircle of the outside diameter of the pipe, leaving a flat edge for a foot to keep the pipe from rolling. The other end of the pipe was ground flat and smoothed off by rubbing on No. 400A grit emery paper laid on a flat plate glass surface. A five-inch disc of plate glass was cut for a window and vacuum seal for the open end of the pipe.

A piece of transite two inches by five and one-half inches was made into a heater by laying ribbon nicrome wire in V's on one surface until 30 inches had been used. This was cemented down with a thin layer of alundum cement. The two ends of the wire were secured to 0.125 inch brass bolts for the cement connection.

This heater was supported on two paraffined plywood rockers so that when the assembly was inserted into the



pipe the upper face of the transite strip containing the heating element was about one and one-half inches above the lower inside surface of the pipe.

Two 0.3225-inch holes were drilled in the pipe, 180 degrees apart and about one inch from the front end.

(*Continued on page 434.*)

A USEFUL GRAPHIC REPRESENTATION OF IONIC RADII

THERALD MOELLER *University of Illinois, Urbana, Illinois*

THE increasing use of the concept of ionic radii as a teaching tool in the explanation of many of the phenomena of inorganic chemistry warrants a presentation which is not only readily apparent to the student but which is also useful in comparing and contrasting the values for the various ions. The several excellent sets of tabulated data (*1*, *2*, *3*, *4*) existing in the literature do not, unfortunately, accomplish this, nor have those plots of ionic radii against atomic numbers which have appeared (*1*, *2*, *3*)[1] done more than emphasize the periodic nature of the ionic radii.

The ionic radius-atomic number plot given in the figure is offered in an attempt to overcome this objection. In this plot, all of the ions within a given periodic group are of the same valence (designated with the group number and subgroup letter at the right) and each group is subdivided into its two subgroups. The use of solid lines connecting the members in each subgroup within a main group then makes it possible to compare the ions of each group as such as well as to observe the differences and similarities existing between two or more different groups.

Included in the figure, in addition to radii for the positive ions of charge types characteristic of the periodic groups, are some values for negative ions in Groups IV to VII. Absent from the compilation are the members of Group VIII (because of the existence of no common characteristic charge type within this group) and included for purposes of comparison are such purely hypothetical ions as F^{+7}. The values used in the construction of this plot are from the theoretical data calculated by Pauling (*1*, *3*) except for the rare earth elements where the values given by Goldschmidt (*2*) are used. The periodic characteristics of the ionic radii are shown by dotted lines.

Inasmuch as the applications of such a chart are so widely varied and dependent upon the problems under consideration, they need not be discussed here. However, the close parallels between the members of the "A" families and between the members of the "B" families as well as the divergencies between the "A" and "B" families within a given periodic group merit mention.

[1] Exceptional is that of Hildebrand (*5*), but the representation given is somewhat different from that reported here.

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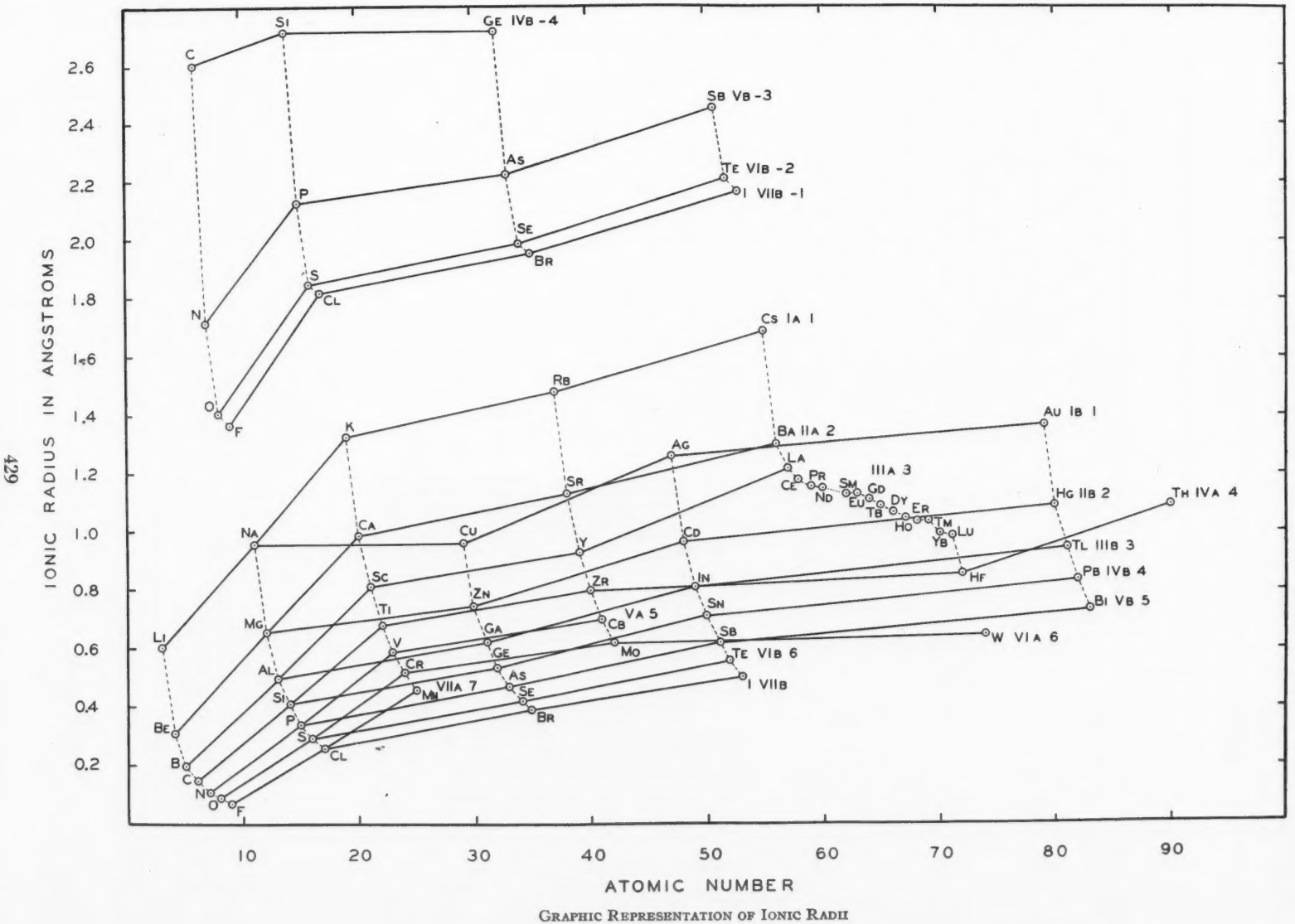
(1) PAULING, "The sizes of ions and the structures of ionic crystals," *J. Am. Chem. Soc.*, **49**, 765 (1927).
(2) GOLDSCHMIDT, "Krystallbau und chemische Zusammensetzung," *Ber.*, **60**, 1263 (1927).
(3) PAULING, "The sizes of ions and their influence on the properties of salt-like compounds," *Z. Krist.*, **67**, 377 (1928).
(4) ZACHARAISEN, "A set of empirical crystal radii for ions with inert gas configuration," *Ibid.*, **80**, 137 (1931).
(5) HILDEBRAND, "Principles of chemistry," 4th ed., The Macmillan Company, New York City, **1940**, p. 267.

Editors Outlook

(*Continued from page 401.*)

the loan provisions are a necessary part of the long range plan. Many had hoped for outright scholarships, and the loan scheme was a frank compromise. In many quarters there is an unfortunate student prejudice against going into debt to finance an education. This is founded upon a false sense of values. It must be pointed out that our whole economic structure is founded upon borrowing and repayment. A storekeeper does not hesitate to borrow at the bank in order to stock his shelves. Otherwise he might have nothing to sell. A college education is the student's method of stocking *his* shelves, and he should not hesitate to borrow money for this purpose, in order that he may sell at a profit later. When an employer hires a man he is effectively investing money in him. If one is not willing to invest money in *himself*, in order to prepare for the job, why should he expect someone else to invest in him?

IT WILL be noticed that the mast-head page carries a new item this month. The JOURNAL OF CHEMICAL EDUCATION has been made the official organ of the Division of the History of Chemistry. While the Division of Chemical Education still retains the full right and responsibility for publication, THE JOURNAL now has an explicit duty to both divisions. As a matter of fact, this merely regularizes a situation which has been in existence since the foundation of THE JOURNAL, when the History Division agreed to lend its support rather than establish another organ of publication. There was always some doubt, however, as to the proper disposition of papers presented before that division, a doubt which need exist no longer.



GRAPHIC REPRESENTATION OF IONIC RADII

Plexiglas and other Acrylic Resins[1]

CHARLES B. WOOSTER

Rohm and Haas Company, Philadelphia, Pennsylvania

WITH THE priority restriction on the general use of metals of the current war effort, rapid expansion in the use of plastics has been given renewed impetus. Today's newspaper carries the story of the plastic airplane, and of the plastic automobile to come. As we have had a stone age, and a bronze age, and an iron age, are we now entering the "plastic age?"

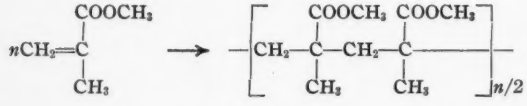
Such a grandiose view of the importance of plastics can be safely doubted. For plastics do have certain definite and serious limitations with respect to a number of important uses. When the strength, or hardness, or weight of steel is essential, and when conductivity of heat or electricity is required, plastics cannot be used. When lightness, transparency, heat, sound, and electrical insulation, or ease of fabrication of finished pieces on a mass production scale are the critical factors, plastics offer great promise.

Courtesy of Rohm and Haas
PLEXIGLAS BOMBER NOSE

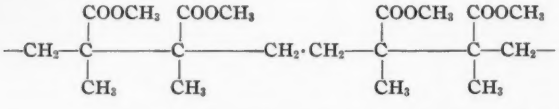
In this paper, consideration will be given a single group of plastics—the acrylic resins. These materials are all thermoplastic. Unlike the thermosetting resins, they do not undergo further chemical change when moderately heated, but merely soften and return again to their original state on cooling. They are relative newcomers to the field, and are, as yet, more expensive to prepare than the average synthetic resin. Nevertheless, they possess such a remarkable degree of colorless transparency and chemical stability, accompanied by hardness and light weight, that they have found extensive application wherever considerations of quality were more important than price alone. Among such applications are airplane windows, automobile safety glass, unbreakable spectacles, dentures, textile and leather finishes, synthetic rubber, and even for setting the permanent waves which are such an essential feature of the feminine coiffure.

It is clear that the value of a new plastic is determined largely by its applicability for particular uses, and it is true that such applicability is usually determined more by its physical than its chemical properties. However, since the physical properties are ultimately determined by the chemical structure, structure will be the starting point of the discussion.

The acrylic resins are prepared by polymerization of acrylic or methacrylic acids, or their related derivatives. This process is a true addition polymerization (not a condensation reaction) and the polymeric products contain all the constituents of the monomeric molecules. Thus, the polymerization of methyl methacrylate (methyl α-methyl acrylate) may be approximately summarized as follows:

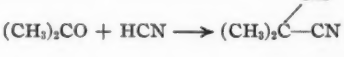


The precise nature of the terminal groups is unknown, as is also the arrangement of the individual units in the chain, which may be uniformly "head to tail" as indicated above, or "head to head, tail to tail" as indicated below:



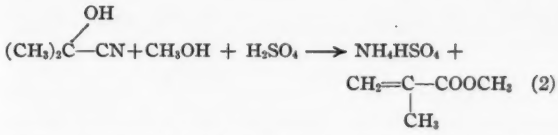
or various possible permutations of these two types of combination. Available information regarding related polymers indicates that the formation of chains with a uniform structural pattern is entirely possible—random orientation of the chain units is not a necessary result of the polymerization process.

The monomers are prepared by reactions of the type familiar to the elementary text of organic chemistry: methyl methacrylate from acetone, cyanide, and methanol:

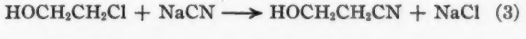


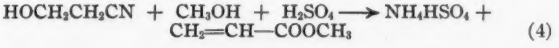
(1)

[1] Address given at the Third Summer Conference of the New England Association of Chemistry Teachers, University of Connecticut, Storrs, Connecticut, August 12, 1941.

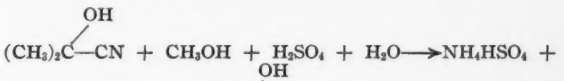


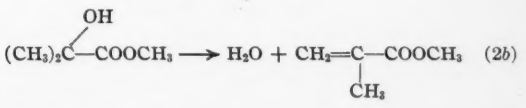
methyl acrylate from ethylene chlorohydrin, cyanide, and methanol:





In both cases, the second step involves a combination of three typical reactions: hydrolysis, esterification and dehydration. Of course, these methods are subject to various modifications in practice. For instance, reaction (2) is sometimes carried out in one step as suggested by the equation, and also in two steps:



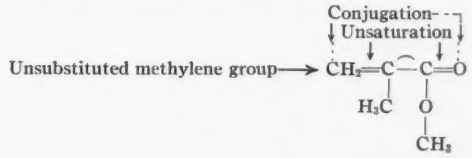


However, the equations given are fundamentally correct and also typify the general method of preparing other derivatives of acrylic and methacrylic acids.

It is sometimes interesting to consider the original sources of our synthetic materials. The principal constituent of Plexiglas and related sheet resins is polymethyl methacrylate. Since synthetic methanol, cyanide, and acetone may all be obtained from coal, it is possible to prepare poly-methyl methacrylate in such a way as to utilize exclusively coal, air, and water to supply all the atoms in the completed polymer molecule. By another method, the polymer molecule might be made by using wood alcohol and acetone from wood distillation. This would provide a transparent sheet which was 88 per cent wood. Even this figure could be increased, up to 100 per cent, by preparing the cyanide from wood charcoal. Again one might use poly-ethyl methacrylate, comprised of 89 per cent acetone and ethanol derived from the fermentation of corn starch, or from molasses.

What is actually used depends entirely on the price. All the cyanide is doubtlessly prepared direct from carbon; most of the methanol is probably synthetic; some of the acetone may be prepared by fermentation, some is prepared from petroleum. The ethylene chlorohydrin used for acrylate manufacture is obtained from ethylene derived from cracking natural gas or petroleum, to a large extent.

A discussion of the detailed mechanism of the polymerization process is made difficult by lack of knowledge at many points. However, unsaturation is an essential structural requirement for addition polymerization, and ease of polymerization is generally promoted by conjugation and by absence of substituent loading at one end of the unsaturated linkage. It is clear that the acrylic and methacrylic esters possess all of these features:



A partially polymerized reaction mixture consists almost exclusively of monomer molecules and highly

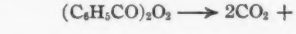
Courtesy of Rohm and Haas

PLEXIGLAS CONTACT LENSES

polymeric molecules. The absence of appreciable quantities of dimers, trimers, and similar low polymers, as well as the incapacity for further reaction shown by the polymer molecules actually present, renders most improbable the hypothesis that these polymerizations proceed by a series of independent stepwise addition reactions. It is much more likely that the process is a chain reaction. For the uncatalyzed polymerization, a variety of chain reaction types are possible, but decisive information obtained under such conditions is lacking. In practice catalysts are used, and a part of the polymer certainly results from catalyzed reactions, although it is possible that uncatalyzed reactions may take place simultaneously.

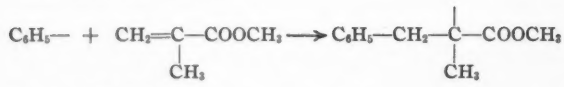
The following equations represent one possible mechanism of the polymerization process, using benzoyl peroxide as a catalyst:

1. *Catalyst Decomposition*



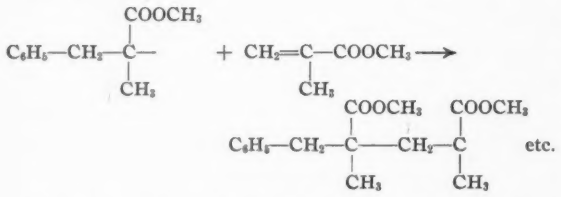
Spontaneous thermal decomposition of the catalyst probably follows this course in part, since carbon dioxide and biphenyl are among the products isolated.

2. Chain Initiation



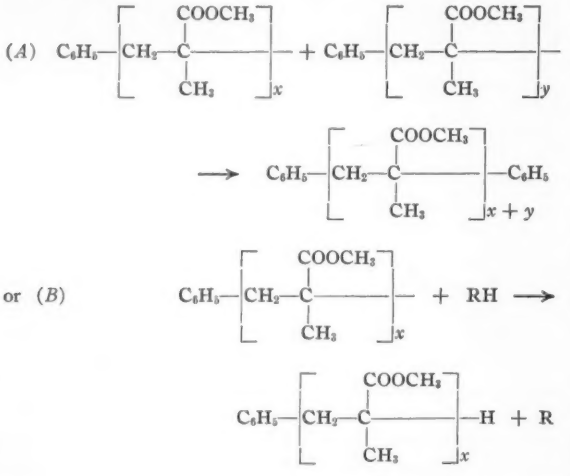
The details illustrated are speculative.

3. Chain Growth



This step is not limited to the growth of chains from identical molecules. If mixtures of monomers are used, the radical formed from one monomer may add to a molecule of the other monomer. The resulting polymeric molecule comprised of units of *both* monomers is called a copolymer. It might be suspected that the free radicals, once formed, could attack and utilize in chain growth a limited number of unsaturated molecules of a type not sufficiently reactive to form high polymers by themselves. This possibility may also be realized and is sometimes distinguished by the term hetero-polymerization.

4. Chain Termination



RH represents a substance whose structure permits it to lose hydrogen and yield a stable molecule. Such materials may be present as impurities; and it is also possible that another growing chain may act in this capacity—losing hydrogen and forming a double bond. Substances capable of combining with free radicals in such a manner as not to generate a new free radical are known to be powerful inhibitors of the polymerization process.

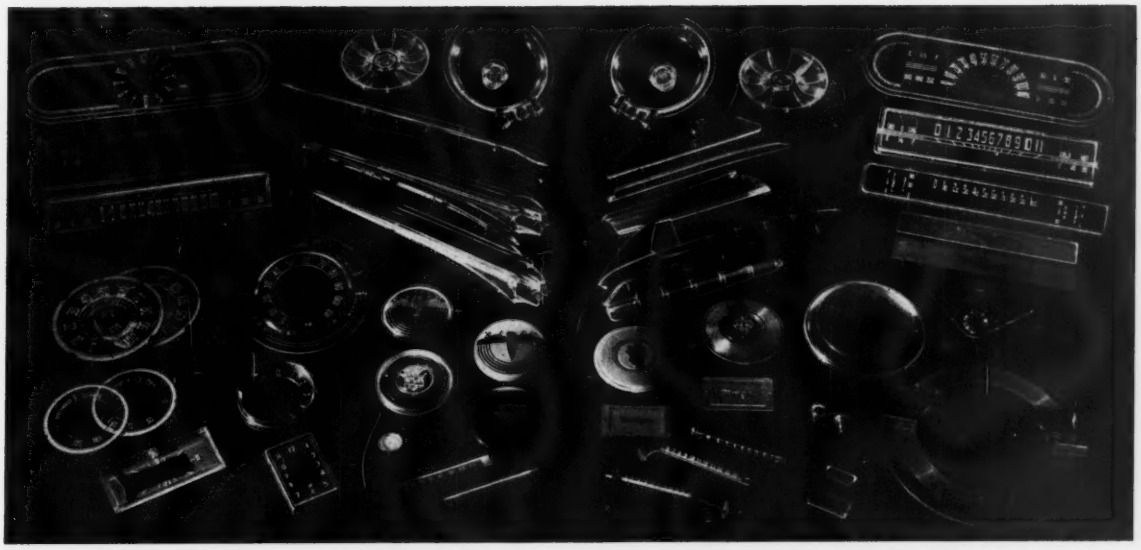
These equations by no means represent a thoroughly established mechanism, but are useful to illustrate one possible interpretation of certain general features which characterize the process. One obvious alternative, for instance, is the formation of an intermediate, unstable, and highly reactive oxidation product (peroxide or ozonide) instead of the free radical in the chain initiation step. The lack of experimental evidence at present renders it unprofitable to consider in detail all the possible alternative mechanisms. However, it may be noted that the polymerization kinetics of methacrylic esters in moderately concentrated toluene solutions are in agreement with a mechanism of the type illustrated by equations 1, 2, 3, and 4*A*, whereas the polymerization of acrylic acid in dilute aqueous solution appears to involve a first order termination reaction such as is illustrated by equation 4*B* when the substance RH is present in high concentration.

Plexiglas is known as a *cast* acrylic resin. This means that the polymerization process itself is carried out in a mold and the monomer is transformed directly into the polymer in its final form as sheet, rod, or tube. When the polymerization rate is controlled with sufficient care to prevent formation of bubbles, and other defects, this yields a product with the highest obtainable degree of uniformity. The product is especially noted for its high degree of colorless transparency, as well as its toughness, strength, and flexibility. The refractive index of Plexiglas, $n_D = 1.4885$, is but slightly different from that of good optical glass (1.51–1.53). Thus, experimental lenses, machined from Plexiglas, may be used to determine the most suitable mold design for silicate glass. Spectacle lenses of Plexiglas, itself, have proved light and accurate as well as resistant to breakage.

The light transmission of a material is limited by its refractive index. For Plexiglas, the theoretical limit is 92.3 per cent, the remaining 7.7 per cent representing unavoidable reflection. (The limit for glass is somewhat lower.) Since the transmission of Plexiglas actually measures 92 per cent in the visible range (3600–7200A.), it does not selectively absorb or reflect much light. Transparency to X-rays makes it useful as splints, through which X-ray photos of knitting bones may be taken.

The most extensive use of Plexiglas is in airplane construction where it has proved invaluable for windshields, nose pieces, observation hatches, etc., because of its combination of transparency, freedom from surface irregularities, high impact resistance, and light weight, as well as its workability. It can be machined, sawed, and drilled with woodworking tools, and can easily be formed at the moderate temperature obtained in an ordinary oven.

In this connection, it is evident that an appropriate softening temperature range is a desirable quality, and the possibilities of adapting resins to specific uses is illustrated by a brief discussion of methods of obtaining a desired softening temperature. The final product of the polymerization of a pure monomer is not a pure compound, but a mixture of similar molecules of varying sizes. It is possible by changing the conditions of



Courtesy of Rohm and Haas

CRYSTALITE MOLDINGS USED IN THE NEW AUTOMOBILES

polymerization to vary somewhat the average molecular weight of the product and, in consequence, its physical properties, including the softening temperature. However, there are definite limits to the variation which can be achieved successfully in this way. It should be clearly recognized that the usual acrylic polymers are always formed directly from the monomer. Such polymer preparations when free from monomer are incapable of further polmerization or curing. When moderately heated they are reversibly softened, when strongly heated they are depolymerized.

Wide variations in polymer properties may accompany the use of different, but related monomers. Thus, acrylic ester polymers are generally softer than corresponding methacrylic ester polymers, and the softness in either case increases with increasing size of the alcoholic radical. Methyl methacrylate yields the hardest polymer of the two ester series. In fact, its softening temperature is somewhat too high for general use.

To reduce this softening temperature, we can use a plasticizer—a non-volatile solvent incorporated with the monomer before polymerization and retained in a sort of solution in the finished polymer. In a rather extreme case, the result would resemble the relationship between a Jello dessert and the original gelatin. The former is highly plasticized with water. A proper choice of plasticizer may give a reasonably satisfactory result—a poor choice may result in bleeding (gradual oozing of the plasticizer), crazing due to gradual evaporation of the plasticizer, and other similar difficulties.

A mixture of polymers would seem to be an obvious recourse, but is unsuccessful due to the fact that high polymers of even closely related structures show very limited miscibilities. On the other hand, the objective can be achieved by the process of copolymerization—polymerizing monomer mixtures instead of attempting to mix finished polymers. This is very successful. Both plasticization and copolymerization are now used industrially in the preparation of acrylic resin sheets.

The casting process does not lend itself readily to the use of intricate molds and the mass production of duplicate articles is best accomplished by the use of a molding powder known as Crystalite. This is not really a powder, but is polymer in the form of tiny spheres which can be prepared to be suitable for molding by either the compression or the injection method. In either case, of course, the polymer particles are heated above the softening temperature to cause them to coalesce and copy the form of the mold. Such molded articles are in extensive use as radiator ornaments, radio and automobile dials, artificial jewels, brush backs, gage glasses, goggle lenses, etc.

A slight variation of this process is used in denture manufacture—the polymer particles are mixed with monomer to form a paste and then set by polymerizing the monomer. The most recent development is acrylic resin teeth, which are said to feel better and "click" less than the usual artificial teeth.

Acrylic polymers are prepared in solution in organic solvents for use in varnishes and lacquers and especially in the production of the laminated safety glass, Plexite. They are prepared in aqueous emulsion for use as leather and textile coatings.

The effect of variations in chemical structure is very evident in the polyacrylic acids, some of which are completely water soluble, and are used in the form of sodium salts on textiles. Their most striking property is the extraordinarily high viscosity exhibited by relatively dilute aqueous solutions.

On the other hand, polyacrylonitrile is very insoluble in all ordinary solvents. So far, no direct use of this material has been made, but the fact that similar solvent resistance is imparted to its copolymers with butadiene has made acrylonitrile an important raw material in the manufacture of the solvent-resistant synthetic rubbers of the type of Buna N or Perbunan.

DEMONSTRATION KITS

College sample kits consisting of a 2-ounce sample of acrylic ester monomer, a 2-ounce sample of compression Crystalite, samples of cast Plexiglas, and of colored molded Crystalite, together with suggestions for lecture demonstrations are available for chemistry teachers. Requests should be sent to the Rohm and Haas Company, 222 W. Washington Square, Philadelphia, Pennsylvania.

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A LOW TEMPERATURE VACUUM DRYING APPARATUS

(*Continued from page 427.*)

These holes were set 45 degrees from the vertical line so that the short lengths of 0.3225-inch copper tubing soldered to them and given right angle bends would come at the upper and lower corners of the square refrigerator compartment when the pipe was inserted.

The upper tube is for the vacuum line connection and the lower tube carries two No. 18 rubber-covered wires to bring current to the heater. These wires were sealed vacuum tight by pouring a hot cement of rosin and asphalt into the copper tube. The details can be seen in the figure.

The whole assembly is inserted into the tray compartment; the vacuum and electric lines can be run up through holes drilled in the floor of the refrigerator.

A glass dish of 125-cc. capacity one and one-quarter inches wide by five inches long was found in a ten cent store and served as the evaporating tray when placed on the heater. A tiny two-inch thermometer off an old Tycos hair hydrometer was held upright by means of rubber bands in the evaporator to measure solution temperatures during the evaporation.

The five-inch circular glass plate was placed over the ground edge of the pipe which had previously been smeared with stopcock grease, the vacuum and electric lines were connected, the pump started, and the refrigerator closed.

Since the heating unit has a resistance of five ohms it is used in series with a lamp socket into which various lamps can be screwed to change the current. With 150-watt and 200-watt lights, the current was 1.2 and 1.6 amperes, respectively, and from the heat formula:

$$\text{Calories} = \frac{I^2R}{4.18}$$

we thus obtained 1.7 and 3.0 cal. per second.

The following table indicates the results that could be obtained with this simple equipment.

TABLE 1

Material	*Series Light*	*Temperature of Solution, °C.*	*Vacuum Pressure, Mm.*	*Loss H_2O per hour*
Distilled water	150 W	2–8	3–4	5.3
	200 W	9–10	6–7	8.3
10% sucrose	150 W	5–4	5–6	5.6
	200 W	10–11	8–9	8.3
10% sodium chloride	150 W			
	200 W	5–10	4–5	7.4
Fresh egg whites	150 W			
	200 W	4–9	5–6	6.0

In all cases with the 150-watt light in series the evaporated water froze out on the walls of the pipe. Sometimes when using the 200-watt light all of the water did not freeze out but collected in a pool in the bottom of the pipe. The temperature of the tray compartment of the refrigerator controls to a great extent the efficiency of the apparatus and with good cooling and low vacuum, five grams of H_2O can be evaporated per hour at a temperature of 2°C. or less.

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BUFFALO CONFERENCE ON EXAMINATIONS

THE SUCCESS of the National Testing Program depends upon the joint effort of a large number of individuals and institutions, in both the construction and use of the examinations. A test must be representative of what is actually being taught by the teachers; further, it must be of greater service to the professor who uses it than a test of his own construction.

In an endeavor to make the Cooperative Tests meet these requirements, a conference on testing is being sponsored by the Committee on Examinations and Tests. A very successful meeting of one week was held last year at the University of Chicago. This year a two-day conference, on September 5 and 6, will precede the American Chemical Society meeting at Buffalo. It is hoped that those interested in the national testing program or in the construction of tests in General, Qualitative, Organic, or Physical Chemistry will take advantage of this opportunity.

Cosmetics

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SINCE the passage of the new Federal Food, Drug and Cosmetic Act of 1938, the entire new field of cosmetics has been added to the responsibilities of the Food and Drug Administration of the National Security Agency at Washington.

Under this law, the term *cosmetic* is understood to cover any substance, preparation, device, or treatment, intended to cleanse, to alter the appearance, or to promote the attractiveness of the person. Thus, instead of being limited to would-be glamorous and often lurid lipstick and other items of facial make-up, it includes all creams, lotions, colorings, and powders for face, scalp, hair, and nails; such borderline preparations as depilatories, deodorants, and dentifrices; artificial hair, teeth, eyes, and limbs; perfumes and soaps; hairdressing, bathing, shaving, massage, plastic surgery, and embalming. Everything, in a word, used by both men and women whether for elaborate treatments in the barber and beauty shops, or at home for the more simple rites of personal grooming.

The art of compounding cosmetic preparations and applying them is almost as old as recorded history, but in modern times the art cannot be dissociated from the science. Obviously, the information required for the successful planning and prosecution of all the cosmetic preparations and treatments listed above draws from many branches of science besides chemistry—from physics, for instance, and many subdivisions of biology.

As the skin is a living organ of the body, the substances that are applied to it or to its appendages—the hair and nails—must be harmless. Since only certain substances can be used to produce certain effects, the range of possibilities for each kind of preparation cannot be wide, so there should not be much mystery about the composition of the various cosmetic products.

The materials used in cosmetics are almost entirely organic compounds, and instead of the natural animal and vegetable substances of which these products were made in earlier times, many now contain only active principles or synthetic organic compounds. Since the average textbook of elementary chemistry is singularly lacking in references to cosmetics as a possible field of applied chemistry, an attempt will be made here to show how cosmetics may be fitted into the usual presentation.

COSMETICS FOR THE SKIN

Preparations for the skin comprise everything used to cleanse, beautify, or recondition it; namely: creams, lotions, powders, make-up, accessories for the bath, and items for personal hygiene. Manicure preparations may also be considered here.

Creams represent the largest group of cosmetics for the skin. They seem to exist in ever-increasing variety, but basically all true creams consist of mixtures of oily and watery substances, blended into a permanent suspension called an *emulsion*.

Two types of emulsion are possible: water-in-oil (abbreviated *W/O*) and oil-in-water (*O/W*). The component that is broken up into globules is said to be in the *inner*, or *dispersed* phase; while the other liquid is said to be in the *outer*, or *continuous* phase. Since even the most vigorous and prolonged agitation does not prevent the eventual separation of naturally non-miscible substances, a compound called an emulsifying agent is added to the mixture as a binder. The nature of an emulsion (*e. g.*, various commercial creams, bought in the market) can be tested by an electric current. If the substance will carry the current, the watery phase is outside; if not, the oil is outside.

The oily or fatty ingredients of a cream vary with the purpose intended. Among the substances used are beeswax, spermaceti (whale), lanolin (sheep's wool), olive, castor, and almond oils, cacao butter, and various fatty acids, similar to those used in making soaps. In recent years, proprietary mixtures (called *absorption bases*), synthetic waxes, and especially mineral oils and waxes (from petroleum) have been increasingly used.

The other phase of the emulsion may be pure water, or solutions of various compounds, intended to produce certain effects; *i. e.*, bleach, contract, stimulate, or cool the skin. The emulsifying agent may be a simple alkali, like borax, or some of the more complicated synthetic organic alkaline compounds.

According to their functions, creams fall roughly into three classes: cleansers, emollients, and finishers. Technically, any cream that is made at low temperatures may be called a "cold cream," but the product best known by this name is the lineal descendant of one first made by Galen, a physician in Rome during the second century, A.D. Reference books and formularies abound in recipes for cold cream. The earlier recipes have been considerably modified in recent years, chiefly by the substitution of mineral oil for some of the organic fats and waxes, which made the product relatively stiff.

Cleansing creams should meet certain definite specifications; *i. e.*, they should melt quickly, spread easily, not penetrate the skin, and leave no greasy feeling after removal. Most manufacturers make at least two types of cleanser, intended for dry and for oily skin. An extremely popular type, especially suited for the latter, is the so-called "quick-liquefying cream," which is not really a "cream" at all, but simply a mixture of

mineral oil products, with the addition of a little perfume.

Emollient creams also should meet definite specifications; *i. e.*, they should penetrate the skin, yet allow free lubrication during application, and effectively soften the skin. Hence they consist largely of animal fats (principally lanolin) or their derivatives. Many special creams—astringent, bleaching, corrective, etc.—have a base of this type, because the active ingredients are thus carried into the skin itself.

Finishing creams are used principally to give a smooth surface as a foundation for make-up. The "vanishing cream" type consists mainly of an emulsion of stearic acid and water, although modern recipes admit of many modifications. This cream does not really vanish; it simply spreads over the skin, in a thin, soaplike film. The other type of finisher, so extremely popular now, has a base similar to that of medicinal ointment, in cream or stick form, to which suitable pigments are added.

To make a successful cream, the ingredients should be mixed at just the right temperature, and thoroughly blended. In factories, this is accomplished by the most efficient devices in large kettles, and the mixture is further "homogenized" by treatment in especially designed mills. To make a sample in the laboratory, a mechanical device, such as an egg beater attached to the cover of a glass bowl, gives far better results than the most patient and persistent stirring by hand.

To prevent rancidity in creams, various preservatives and "anti-oxidants" are used, and in this field the more familiar older type of preservative has given way to many new and interesting synthetic organic compounds.

Make-up comprises the preparations used to enhance the natural coloring of the complexion, or "make up" for a lack of it. The term covers face powder, and colorings for cheeks, lips, and around the eyes.

Face powder now consists almost entirely of metallic products. Starches—long the stand-by, and still found in many imported powders—have been practically abandoned in the better American products. Like creams, face powders should be varied in composition for the type of skin (*i. e.*, dry or oily), and should meet certain qualifications:

Opacity	produced by zinc oxide or titanium dioxide
Ease of spreading	produced by talc
Adherence	produced by calcium, zinc, magnesium stearate; kaolin
Fineness	produced by grinding through fine screens; blowing through air tower
Absorbency	produced by calcium or magnesium carbonate

The last-named ingredients serve a double purpose: to hold the perfume and coloring, and to take up oil and moisture on the skin.

"Light-" or "heavy-weight," as applied to face powder, refers to opacity or covering power, not to mass. A light powder is one that dusts on and off relatively easily; it is more suited to a dry skin which may be more or less rough. Heavy powder is better suited to the oily skin, which is usually smooth and which may require relatively more powder to produce the currently desired dull finish.

Students of chemistry will realize that all the compounds mentioned are white. A rough idea of the purity of the ingredients of a powder can be obtained from the degree of whiteness of the various substances. To make them into the delicately tinted finished products, suitable for all shades of skin, a small percentage of earthy pigments, lakes (metallic-organic dyes), or organic pigments are skilfully blended into the basic mixtures. Under the new federal law, no coloring may be used unless it comes from batches certified by the Food and Drug Administration.

Face powders on the market may be tested for starch by the familiar iodine test. The lightest obtainable shades should be used.

Talcum powder, as used after bathing or shaving, for babies' toilet, for the feet, etc., consists principally of talc with the addition of absorbent substances, mild antiseptics, light coloring, or other ingredients depending on the specific purpose intended.

Rouge is made in three forms: cream, paste, and compact powder. The base of the creamy products contains many of the substances described under creams; commonly, petrolatum ("vaseline") and lanolin, with a fair percentage of stiffer waxes. Colors must be well chosen and perfectly incorporated. Paste rouge is made of similar mixtures, without water.

Powder rouge contains ingredients similar to those in face powders, with the coloring worked in to make a perfectly homogeneous mixture. The little cakes are made by pressing and stamping, either wet or dry, and either with or without the addition of a binding substance.

Lipsticks are made of the same bases as the cream or paste rouge, with relatively more of the stiffening waxes.

Eye Cosmetics are now subject to the most rigid control, particularly in the matter of the colorings used. Crayons for the eyebrows may be made up like elongated lipsticks of solid waxy substances; or as slender cores for wooden pencils. Shadow for the orbital region is usually a cream or ointment containing blue, violet, green, brown, or other appropriate pigments. Under the new law, organic dyes may not be used.

Eyelash colorings may be either temporary or permanent. The former, commonly called *mascara*, consists of a soaplike cake of synthetic and natural waxes, with the addition of carbon black, or brown, blue, or green pigment. It is applied like a paint with water and a brush. Permanent colorings consist of a harmless metallic dye (silver nitrate) and a developer (see section on hair dyes). Organic dyes may not be used.

Lotions are water or water-alcohol solutions which vary widely depending on the purpose for which they are intended. Thus, lotions for toning or stimulating

the skin usually contain mild irritants, such as natural balsams, or synthetic organic compounds. Bleaching lotions usually contain hydrogen peroxide or other substances that will liberate oxygen. Medicated lotions serve a variety of purposes, but they are usually indicated for clearing up minor eruptions of the skin. They may contain solutions or suspensions of zinc compounds, certain organic compounds, and a small percentage of phenol ("carbolic acid") or a related compound, to make them smell "antiseptic." Most cosmetic lotions are delicately tinted and perfumed. Depending on the claims made for them, lotions may automatically remove themselves from cosmetics into the classification of drugs, which requires a declaration of ingredients on labels.

COSMETICS FOR THE HANDS

Hand Lotions may be simple solutions of rose water and glycerine; dilute mucilages from natural gums; or dilute creamy fluids, similar in composition to the stearic acid creams described in another section. They are effective all-year-round aids, intended either to take up excess moisture (as after washing the hands) and prevent chapping of the skin, or simply to make the hands (also arms and legs) smooth by the spreading of a light protective coating.

Cuticle Solvents are 1 per cent to 2 per cent solutions of potassium hydroxide; their purpose is to soften the skin around the nails so that it can safely be pushed back.

Nail Bleaches contain hydrogen peroxide or dilute solutions of mild organic acids, such as citric, oxalic, or tartaric.

Nail White, in powder, cream, or stick, contains familiar zinc or titanium compounds.

Nail Polish may be in the form of powder, waxy cake or stick, clear or creamy lacquer. The powder (loose or compact) consists of a mild abrasive, such as stannous oxide. The cake or stick contains natural or synthetic waxes and (usually red or pink) coloring. The increasingly popular lacquers are carefully blended mixtures of nitrocellulose, compounds of aliphatic acids, or some of the newer synthetic resins ("plastics"), with other ingredients selected to assure free flow, flexibility of the film, well-timed evaporation, and good adherence to the nail. The appearance of "creamy" lacquer is due to suspended pigment (usually white).

Polish Removers consist of mixtures of organic solvents, similar to those used in compounding the lacquers. The simplest and most familiar are ethyl acetate and acetone, but many related aliphatic compounds are now in common use. Because all these liquids are extremely drying to the nails and surrounding skin, a small percentage of animal or vegetable oil, or some other fatty substance is now usually added.

COSMETICS FOR PERSONAL HYGIENE

Under products for personal hygiene may be included soaps, accessories for the bath, deodorants, depilatories, preparations for the mouth, and for sun-tan.

Toilet Soaps must receive special care in manufacture. From the standpoint of cosmetics, all soaps must be judged in terms of their action on the skin. A nice-looking soap may be "100 per cent pure" as far as its ingredients go and yet not be good for the skin.

In general, soaps made of olive oil are the best for the skin, but they are not appreciated fully because they produce relatively little lather. Hence, most toilet soaps are made with a varying percentage of coconut oil, which makes a product that lathers profusely. All-coconut oil soaps are admittedly harsh and occasionally irritating to a sensitive skin.

Superfatted soaps, containing free fatty substances, might be beneficial, but frequently are not effective because of the hard water so prevalent throughout the country. The excess of fatty acid interferes with the hydrolysis of the soap and thus prevents proper cleansing.

Bath Salts consist of familiar mild alkaline compounds, usually delicately tinted and perfumed. Their real function should be to soften the water, so sodium sesquicarbonate and several sodium compounds of phosphoric acids are widely used in manufacturing them.

Bath Oils usually consist of a sulfonated oil, made by treating olive or castor oil with sulfuric acid. They are usually colored and may be heavily perfumed with (usually synthetic) pine. These products are generally extremely drying to the skin. Foaming oils (and powder or granules intended for the same purpose) consist of, or contain, higher fatty alcohols or derivatives, similarly treated with sulfuric acid. All these compounds are adapted from products used in the textile industry.

Deodorants are of two types, depending on whether they actually stop perspiration or merely deodorize the sweat as it reaches the skin. The former (more properly called *anti-perspirants*) consist of strong astringents, generally compounds of aluminum and zinc which deflect the sweat from the places of application to other areas of the skin. They may be in the form of liquids, or creams, similar to the vanishing creams described in an earlier section. Many important factors must be considered in the compounding of preparations of these types, notably the effect on fabrics as well as on the skin.

Simple deodorants are usually creams, containing mild antiseptics, peroxides, or certain complicated synthetic organic compounds.

Depilatories for the removal of superfluous hair formerly consisted of sulfides of strontium or barium with the addition of a corrosive substance like lime, or inert fillers, such as starch, various silicates, calcium or magnesium carbonate. These preparations were in powder form, to be made into a paste as required for use, and were objectionable both because of the odor of hydrogen sulfide which was always liberated and because they were so commonly irritating to the skin. Newer products, made up as cream, powder, or paste utilize organic compounds of sulfur and are almost entirely free from offensive odor.

Other preparations used for removing hair are more properly called *epilators*, as they pull the hairs out of the skin. These consist of various waxes and resins, of varying degrees of hardness, and their action is entirely mechanical.

As with some of the lotions previously described, deodorants and depilatories, while formerly classed as cosmetics, are on the border line and may be classed as drugs, because they affect some structure (hair) or function (perspiration) of the body.

Oral Preparations include dentrifrices and mouth washes. The former consist of mild abrasives, soapy products, and fillers, occasionally tinted, always flavored pleasantly. Whether in the form of powder, paste, or liquid, their function is only to cleanse the teeth, and thus serve as prophylactics in dental hygiene. Mouth washes are water-alcohol solutions of antiseptic and aromatic compounds, intended to leave the mouth feeling fresh and clean. Also borderline preparations, they may be classed as drugs or as cosmetics depending on the claims made for them.

Sun-Tan preparations have sprung into great popularity in recent years. Depending on the use intended, they fall into three groups: (1) those that prevent sunburn; (2) those that imitate the color of tanned skin; (3) those that heal a burn.

The second group is the simplest, as the preparations are only creams or powders tinted to certain shades. The preventive preparations are either liquids or creams, containing well-chosen compounds that can serve as chemical or physical screens against the harmful ultra-violet rays in sunlight. Many substances are available, and after considerable research by many qualified investigators, it seems to be agreed that the best protective agents are certain complicated synthetic organic compounds, dissolved in alcohol, water, or light oils.

Remedial preparations are really drug products, so we shall not discuss them as cosmetics.

COSMETICS FOR THE HAIR

Cosmetic products for the hair (and scalp) comprise shampoos, lotions, waving preparations, and colorings.

Shampoos are of three kinds: soaps, "soapless," and dry.

Soap shampoos are water solutions of various standard soap bases. For wholesale trade and for sale to barber and beauty shops, shampoo may be sold in beads, flakes, bars, or jelly, to be diluted and stored for use as required. As with toilet soaps, the properties and effects of a shampoo depend on the nature of the base, olive oil soaps being considered the kindest to both hair and scalp. For psychological effect, some percentage of coconut oil is usually incorporated. Many combinations of natural fats and fatty acids, especially some of the newer, higher aliphatic compounds have been investigated with a view to improving shampoos.

Soapless shampoos consist of sulfonated or sulfated fatty compounds, similar to those described under Bath Oils. They have been the subject of many programs of research and much still remains to be done on them. Their ease of operation in hot or cold, hard or soft water gives them a great advantage over soaps; but their too-thorough detergent properties make them not equally successful on all kinds and conditions of hair.

Dry shampoos are either mixtures of powdered soaps, various alkaline detergents, and inert fillers; or organic dry cleansing fluids, such as carbon tetrachloride, isopropyl alcohol, and benzine. The former act only mechanically. The latter, being powerful solvents of grease, may be extremely drying to the hair and irritating to the scalp.

Scalp Preparations may be in the form of lotions or ointments. The former (formerly known as "hair tonics") consist of water or water-alcohol solutions of a variety of ingredients—organic and inorganic—so compounded that application will stimulate the scalp to a point just short of irritation. The components of these preparations have progressed from natural organic substances, such as balsams, crushed flies (cantharides) and ants, through poisonous metallic salts (arsenic and mercury), and now consist largely of synthetic organic compounds, many of them the active principles of long-known natural organic substances.

Ointments are mixtures of oily and fatty compounds, containing the same active ingredients in solid form. Among the substances most commonly used are sulfur (one of the oldest remedies for eruptions of the skin) and zinc (calamine or the oxide).

Claims must be made with caution, or the products go over to drugs.

Waving Preparations are of two distinct kinds:

Permanent waving solutions consist generally of alkaline compounds which can soften the hair and thus help to change the form of it under the heat produced by the waving apparatus. The borax and other sodium compounds originally used for this purpose are now largely replaced by ammonia, alone, as ammonium salts, or in the form of more complicated organic derivatives called *amines*. Various compounds of sulfur have come into use of late, notably the simple or compound sulfites, sulfides, and hydrosulfides.

Alcohol, soaps, and fatty compounds which form nascent soaps, sulfonated oils, and many other compounds also enter into the composition of waving solutions. The whole subject of permanent waving—not only the solutions themselves, but also the exothermic mixtures used for the pads in "machineless waving," and the newest process of "heatless waving"—offers an inviting opportunity for sound research on its interesting problems.

Waving fluids, or setting fluids, consist of mucilage from natural seeds and gums (similar to those in hand lotions), with alcohol, glycerine or related compounds, mild alkalies, and optional perfume and coloring. Their action is entirely mechanical. To prevent deterioration, preservatives and antioxidants are essential, and much good research still remains to be done on these useful products.

Hairdressings, to improve the appearance of the hair, may be mixtures of various fats and waxes; or light mineral oil, colored and perfumed. The former are usually intended to hold the hair in place, while the latter may be used only to make it glossy—hence the name "brilliantine."

The oily substances used in these dressings—and for "oil treatments" in general—present an interesting variety of properties and effects, which should be taken into consideration in compounding them. Animal fats, such as lanolin, tallow, and neatsfoot oil, have the best softening effect on the hair, but make it actually dull. Vegetable oils come next, while mineral oils, which give the most gloss, may eventually be actually drying.

Hair Colorings, using the term in the broad sense for any preparation that effects any change in the shade of the hair, may be either bleaching agents or dyes.

Bleaching is effected best with hydrogen peroxide, using a 5 per cent or 6 per cent solution instead of the usual 3 per cent "drug store" product. The speed and efficacy of the bleach depends upon the volume of oxygen obtainable—roughly, three volumes of oxygen for each per cent of the compound. The properties of the solution come into consideration in the use of a small amount of acid or organic preservative to keep the product at full strength before use; and the addition of concentrated ammonia water (28 per cent) to cause the rapid liberation of the oxygen while it is on the hair.

So-called "white henna" is a trade term used to oblige—and confound—the laity. The white substance is a "hydrated magnesium carbonate" (a mixture of the hydroxide and carbonate), which serves to make paste with hydrogen peroxide and assure that the bleaching agent will stay in the right place during the treatment. As the ultimate shade from all bleaching with hydrogen peroxide is always yellowish, this tinge is often neutralized (to "platinum blonde") by the application of a bluing rinse.

The bleaching—more properly "blanching"—properties of sulfur dioxide are occasionally utilized in preparations for removing dyes. Further application of this principle has been hindered to date by the technical difficulties involved.

Dyes may be either temporary or permanent. The former consist of organic pigments, usually mixed with a mild organic acid. When rinsed over the hair, they impart to it a pretty gloss and a tinge of color which should last until the next shampoo. Many attempts have been made to compound these rinses from the limited range of certified colors for food. The bluing rinses mentioned above (also popular for naturally gray and white hair) now belong almost exclusively to this type of coloring. They are made from various blue and violet organic dyes, rather than the Prussian Blue, formerly used for this purpose.

Permanent dyes may be of three groups:

1. Natural organic substances, such as henna, camomile, the more antiquated indigo and sage, and decoctions of certain nuts and barks.

2. Metallic salts, often dilute solutions of lead, silver, copper, nickel, iron, or bismuth. The underlying principle is the same for most of these preparations: all these elements form dark compounds on exposure to the air. Occasionally one is found with a developer which precipitates a dark-colored sulfide or oxide.

Lead salts (acetate or nitrate) are now usually combined with flowers of sulfur in suspension.

Silver nitrate (occasionally combined with a nickel salt) utilizes the natural darkening tendency of all silver compounds when exposed to light, and also their property of forming dark brown compounds with protein substances. Variation in shade can be effected by the addition of varying amounts of ammonium hydroxide, which holds some of the silver in the form of complex ions. To hasten the action of the dye, a developer is usually included with silver preparations; either sodium thiosulfite (photographers' "hypo"), or pyrogallol, an aromatic organic compound related to phenol.

Copper compounds, often combined with ferric chloride, may be either in solution (usually with a developer), or mixed dry with henna, pyrogallol, and other dyeing substances. This mixture forms the so-called "compound henna."

3. Synthetic organic dyes constitute the most popular and most satisfactory type of product at present. Similar to dyes used for furs, they consist of simple solutions or complex mixtures of aromatic compounds, derived from coal tar, many of them related to phenol and aniline. For maximum efficiency and depth of shade, hydrogen peroxide is used as a developer.

The only disadvantage of these modern dyes is that they belong to the large group of substances that may cause irritation of the skin in sensitive individuals (allergy). Because of this, these dyes are subject to special regulation under the new federal law.

PERFUMES

No discussion of cosmetics would be complete without mention of the perfumes and aromatic materials that contribute so much toward making them attractive.

The compounding of perfumes is recognized as one of the oldest arts, but it, too, has accepted much from science after it was discovered that many of the natural scents of flowers and flavors of fruit could be duplicated in synthetic organic compounds. Both aliphatic and aromatic compounds are utilized, in ever-increasing numbers, a fact that is of significant economic value, because it has brought many prohibitively expensive odors within the means of both manufacturers and the buying public.

The raw materials of perfumes come from many sources, of both animal and vegetable origin, and from every corner of the globe. The production of a seemingly uniform scent in a line of cosmetic products may be made of surprisingly different components. Regardless of how the scent may be named, practically none of the familiar odors is produced by a simple, single essential oil; many of them are extremely com-

plicated and made from both natural and synthetic substances little related to the flower that the blend suggests.

Research on perfumes is a fascinating occupation, but it calls for a keen esthetic sense and other personal characteristics too often lacking in those trained in science.

MANUFACTURING PROCESSES

The compounding of cosmetics is no longer the mysterious, possibly glamorous, occupation it was long believed to be, when "beauty doctors" concocted magic elixirs and pomades in secret rooms and doled them out to desirous, and often designing, ladies. True, there is still some small-scale manufacturing of certain products, stewed up "in a double boiler on the back of the stove," and patiently transferred by hand to bottles, boxes, or jars. But on the whole, the cosmetic industry has shown remarkable enterprise in the utilization of, and the devising of, the most efficient and up-to-date equipment for mass production.

Down to the last detail, steps in the manufacture of various creams, powders, lotions, etc., are worked out by competent engineers. The creams are mixed in glass-lined kettles, equipped with indefatigable stirring devices. The powders are carefully blended, ground in mills, and either sifted through progressively finer screens or blown into impalpable fineness. Lipsticks and other crayons are fashioned in uniform metal molds and assembled by deft hands. All operations of filling, covering, labeling, and wrapping are accomplished in record time by ingenious machines. Altogether, the enterprise of the leaders of the industry in recent years offers a splendid example that could well be emulated by manufacturers of other types of products.

All manufacturers do not make all of their own products. Because of obvious difficulties, rouge, lipsticks, mascara, and nail lacquers are commonly bought from wholesale manufacturers, especially equipped to handle such items. The retail manufacturer may purchase stock preparations, or have various items made up according to his own specifications.

It is hoped that by now the reader will have lost any false notion that "anyone can (or everyone should) make cosmetics." After a long and fascinating history, these products have passed from the hands of ancient priests and physicians through various vicissitudes into the hands of trained scientists, principally chemists.

Putting these products under government control has given them a status, and brought out the fact that the problems in this field are as worthy of investigation and solution as are those of foods and drugs. The solution of any one of these diversified problems can well tax the knowledge and ingenuity of those skilled not only in the many branches of advanced chemistry required for solving them, but also in physics, physiology, dermatology, and histology.

The use of cosmetics can no longer be regarded as a passing fad. They have admittedly come to stay, and the application of cosmetic preparations and treatments in the rites of beautification and good grooming is well on the way to being recognized as a branch of applied science.

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The WPB has just told us that among the many things which we may not make of iron or steel are: Asparagus tongs, beer mugs, casket hardware and memorial tablets, chamber pots and bed trays, coffee roasters, chiropractic tables, dummy police, dinner bells, fly traps, golf bag supports, hair dryers, jelly molds and lobster forks, knitting needles and crochet hooks, mop wringers, park benches, pleasure boats and rolling boardwalk chairs, Sitz baths and rotary door bells, sporting goods and swivel chairs, voting machines and vanity cases, whiskey service sets and siphon chargers. Also—although we aren't quite sure—we think you had better be looking around for a metal-substitute for that mousetrap you were going to invent.

« « « « HIGH-SCHOOL CHEMISTRY » » » »

Chemistry in the Ink Industry

CHARLES R. BRAGDON *Interchemical Corporation, New York City*

AS SHORT a time ago as 1935, a new pictorial weekly, bright with color, meeting the highest standards of printing technic, amazed us by bringing pictures of Saturday news events to newstands and homes in all parts of the country on the following Friday. Previously, national magazines, even with only scanty color "dress-up," had closed their forms from two to six weeks before publication date. To chemistry goes the credit for this time-saving achievement. For chemistry has designed an ink which dries in a second, an ink which uses a solid resin and a rapidly drying solvent, instead of the old slow-drying linseed oil. Three hundred of the higher-grade magazines are now printed by this process. Mail-order catalogs and numerous other printed articles are speedily turned out. Frequently the new ink is adopted more for the richer quality, sharpness, and brightness of the finished work than for the sake of saving time.

A metropolitan newspaper has adopted another radical printing technic. An ink, which is solid at room temperatures, is applied to the paper from heated type-forms supplied with molten ink from a heated fountain by heated distributing-rollers, all at 160–180°F. This ink (a mixture of pigment, wax, and thermoplastic resin) freezes again immediately on application, producing a very good, sharp, and relatively smudge-free print. Ordinary news-inks are merely carbon black and toner (a bluish-black aniline dye), ground in a moderately fluid mineral oil. News-inks "dry" by absorption into the loosely felted fibers of the paper, and the print is certainly not smudge-free! The newer process of solid ink is not more widely used because of mechanical drawbacks.

Other advances in printing technic due to chemistry are everywhere apparent in the big modern printing plants. Contrast the older presses with the new giant, half-human machines. The old presses operate on the sheet-fed, natural-drying system which, in basic principle, is the same system Gutenberg used in the 15th century. The presses stand eight or ten feet high, each on a floor area about eight by sixteen feet. An open steel framework supports one or more pairs of impression cylinders, each with its train of rollers to bring the ink, gradually worked out to a uniform film, from fountain to printing form. At one end of the press is placed a stack of sheets of paper, or "signatures," each sheet about four and a half by six feet, and the stack, edges perfectly aligned, about four feet high. From the top of the stack, automatic fingers, tipped with vacuum cups, deftly pick up the sheets, one by one, and feed them into the press. Passing through the big impression cylinders, one of which carries the type-form, or plate, curved around its surface, they receive a print in one or two colors, and are then delivered to a similar stack at the other end of the press. Dozens of these partly printed stacks are ranged in rows through the room, the top sheet showing the roughly oblong masses of (usually) sixteen pages. Some pages may show only a yellow blur of an unrecognizable picture, to which, by the successive overprinting of red, black, and blue from the carefully adjusted halftones, is added the whole spectrum of color, to bring out the modern full-color reproduction of a photograph or a painting. About eighty sheets a minute can be fed through a press of this style. But when the pile of delivered sheets has reached a height of three or four feet, it must be set aside to allow the ink to dry. And usually a full day or more must elapse before the next operation.

The ink used in this old process consists of pigments ground in thickened linseed oil, the historic and still widely used vehicle material for both typographic and lithographic inks. Linseed oil is the ester of the trihydric alcohol glycerol with a mixture of fatty acids (the carboxyl compounds related to the straight-chain, paraffin hydrocarbons), mostly with 16 and 18 carbon atoms. The fatty acids are of the unsaturated type, meaning that one or more pairs of their carbon atoms are joined by double bonds. When such an unsaturated oil is heated to about 300° to 315°C., interlinkage of these fatty-acid chains begins to take place. With the increase in size of the molecule, viscosity goes up. Thus, by heating for various lengths of time, a series of "litho varnishes" is made, graded by an arbitrary series of numbers from 000 (very thin), 00, 0, and 1 (moderately viscous), on up to 8, which represents a rubbery, almost solid mass. The characteristics of the particular pigment to be used determine the choice of the "litho varnish" or mixture which will, when thoroughly ground with it on a 3- or 5-roller mill, produce proper printing consistency. It must possess sufficient "tack" or stickiness to distribute properly on rollers, plate, and type, and to adhere to the paper without picking off the surface. The impression so made is still wet and sticky; aside from a slight absorption of the thickened oil by the paper fibers, the conversion to dry, adherent, rub-resistant condition must be left to oxidation. Here the double bonds of the fatty acids of the

linseed molecules again come into play (those not already used in building up the larger molecules of the more viscous oil), reaching into the air to take up oxygen and form a new solid compound of considerable toughness, called linoxyn. This is a relatively slow process, even when stimulated by oxygen-carrying metallic salts or soaps (most frequently those of cobalt, lead, or manganese), which are generally incorporated in the ink as catalysts. Printed work must lie spread out for several hours before it can be handled. If the sheets are piled too high, or handled too soon, the ink will smudge. For the sequence of four impressions which provide illustrations in full color, with folding, cutting, binding, etc., about a week must elapse to complete the job.

The modern presses, leviathan affairs, are the latest word in printing craft, and are made possible by the chemical development of improved ink. They rise from the floor well up through the second story—eight or ten feet wide, and thirty or forty feet long. The paper is threaded in a continuous web from a large roll mounted on a shaft at one end, over and under a sequence of guide- and impression-rollers, like thread through a sewing machine. Darting along at a speed of 800 to 1200 feet per minute, the paper is printed continuously, receiving from two to four impressions on each side. The "vehicle" of the ink in this case consists of a solution of a solid, dry resin in a high-boiling organic solvent, which is so slowly volatile at ordinary temperatures that the ink does not thicken up or dry when exposed in thin layers in the distributing system or the impression form. But in the box-like furnace, fired by roaring gas flames, through which the web of paper passes on emerging from the impression cylinders, the solvent volatilizes instantaneously and completely (and even burns), so that the sheet comes out with the print perfectly dry to touch, and smudge-resistant. It seems unbelievable that the paper, too, does not catch fire in this terrific heat (about 900°C.), but it speeds through so fast that it is not even scorched or weakened. It must not be allowed to stop! Quickly it passes through a cooling zone, then immediately to the next impression and furnace-drying; and so on, until printing is complete. The folder and cutter are built in at the delivery end of the press, so that the signatures come out all ready to be assembled, bound, and sent out. By an ingenious device, the outer end of a new roll of paper can be pasted while in fast motion to the tail end of one that is just being used up, so that the presses can be kept in continuous operation, day and night, with a minimum of human attention, during the run of an issue. Thus a streamlined production line turns blank paper into finished magazines or catalogs in a few minutes, multiplies output, and gains remarkably in timeliness of distribution.

Another very recent development in typographic printing has been the introduction of so-called "water-set" inks. In these, also, the binder is a resin; the solvent is a high-boiling, water-miscible organic liquid, from which the resin can be precipitated by adding water. Such inks are "set" and dried without high heat, merely by passing the printed work through a jet of steam or atomized water-spray. Two of the chief advantages of such inks are that they are practically odorless and that they lend themselves readily to waxing, as for bread-wrappers, and other food-product containers—a line of work that consumes a surprising amount of inks.

But what of the kind of ink we usually think of first when "ink" is mentioned—the writing fluid in our fountain pens or ink wells? That goes back to the early days of chemistry, when ferrous sulfate, or "copperas," was dissolved in a decoction of nutgalls (supplying gallic acid, a compound of the same family as tannic acid) in water. The light brown mark left by stroking this out on paper by brush, quill, or pen turned black by oxidation—and faded again, in time, to brown ferric oxide. After the introduction of coal-tar dyes some of the deep blue ones were added to make the fresh writing more easily read, and an ink of this kind is still the standard of the federal specifications. Nowadays many writing fluids are straight dye solutions, sometimes with a small amount of vegetable gum to bind them firmly to the paper. Waterproof drawing inks are dispersions of finely divided carbon, or of dyes containing a binder that becomes insoluble upon drying out. Stamp-pad inks are like writing fluids, with glycerol added to keep them from drying on the pad; and mimeograph inks are more viscous modifications, drying chiefly by penetration into the paper.

These inks include the class which employs water as a solvent; and, while familiar and important, their production is small in comparison with the printing inks, which enable the Graphic Arts to take sixth place among American industries. Printing inks have the general characteristic (possessed also by paints and enamels) of consisting of a coloring agent (pigment or dye), intimately mixed with a non-volatile binder of oily or resinous character, also often containing driers, waxes, solvents, and other materials to impart special properties. But, while the basic ingredients are the same, printing inks differ widely from paints and enamels, and from each other, according to their destined method of application. The three main printing processes are the typographic, planographic, and intaglio, distinguished, respectively, by delivering the impression from raised characters or surfaces, like ordinary type; from areas substantially in the same plane as the surrounding non-printing surface; and from depressions or engraved designs.

The first and most widely used of these, the typographic process, is old and familiar to most of us; but the other two are less well known. The planographic, or lithographic, process has developed from the discovery, made about 100 years ago, that a design made on a smooth stone (Greek "lithos") surface with greasy ink or crayon is receptive to printing inks, which are repelled from the remainder of the surface if it is kept dampened with water, or with a dilute acid solution containing a little water-soluble gum, such as gum

arabic. Later it was found that sheets of zinc or aluminum, or even stainless steel, could be prepared by grinding with sand so that they served in place of the heavy stones. The designs are quickly applied to the sheets by photographic reproduction, and the sheets may readily be mounted on impression cylinders on suitable presses. By taking off the impression first on a rubber blanket, which then transfers it to the sheet of paper, metal, or other material which it is desired to print, the "offset" process becomes extremely versatile, providing the countless decorated cans and containers so familiar today. Lithographic inks are essentially the same in composition as those for typography, except that they are more viscous. In addition, lithographic inks must be made up with pigments, and oils or resins, which do not "bleed" (dissolve) or emulsify readily in contact with the dampening water on the press. Recent introduction of fast-drying vehicles has made possible planographic timesavings similar to those used in typography, described previously.

The third, or intaglio, process developed from the old steel die or copper-plate engraving used for calling-cards, stationery, invitations, etc. The engraved plate is smeared with a "short" ink (one that has little tendency to string out), and the excess cleanly removed by means of a wiping sheet, or sharp scraper blade. Upon then pressing the paper to be printed against the plate, the ink remaining in the depression is picked up. Originally slow, this became the speedy rotogravure process when the engraving was done on a copper cylinder, and the paper fed between it and a pressure cylinder in a continuous web. The ink is made very thin (largely solvent which is highly volatile at ordinary temperatures). It is placed in a fountain into which the revolving impression cylinder dips, picking up a film of which the excess is wiped off by a stationary scraper placed just above the liquid surface. The ink remaining in the depressed portions reaches the paper in a fraction of a second; being composed of solvent, solid binder (resin, nitrocellulose, or bitumen), and coloring matter, it dries instantaneously by evaporation and absorption, and may be followed at once by additional impressions on the same or reverse side. Quickness of solvent release is an important requirement for these binders; gilsonite, nitrocellulose, and certain maleic resins meet it, but many resins are slow in reaching the tack-free state as the solvents evaporate. The brown rotogravure inks used on the pictorial sections of many of our newspapers consist almost entirely of gilsonite or similar bitumen, which doubles in the roles of binder and coloring agent, and a low-boiling petroleum hydrocarbon distillate, sometimes reinforced with a ketone derived from petroleum or natural gas fractions by chemical transformation. The colored inks have been largely based on nitrocellulose, similar to the lacquers which replaced slow-drying oleoresinous finishes on automobiles some years ago; or natural resins, exudations of trees found in the East Indian islands.

Pigmented printing inks applied by the intaglio process have recently invaded an entirely new field, that of textile printing, formerly ruled exclusively by water-soluble dyes. In this older method, coal-tar colors are applied to the cloth in a partially compounded or "intermediate" state, and have to be oxidized, or "coupled" with other dye intermediates, by passing through special baths, steaming processes, etc., in order to complete the reaction which brings out the final color, fixed to or impregnated in the fiber itself in such a way that it is relatively fast to light, washing, and dry-cleaning. These intricate processes make it hard to assure exact duplication of hue from one batch or run to another. The new pigment printing process eliminates the several steps of development of the dye, retaining only the one short heat-curing stage. Sharpness of image is markedly improved, and fastness is as good or better. Synthetic resins have made the process successful by enabling the pigments to be bound so firmly to the cloth, without adversely affecting the softness, that they no longer rub off, as was always the case in earlier attempts along this line.

In making use of the newer synthetic resins, oils, and solvents, ink chemistry has progressed hand in hand with its sister science of paint and varnish chemistry. The pigments that it uses are also of similar type to those used in paints and enamels, and in rubber. However, printing inks demand certain special qualities: high opacity on account of the much thinner films used; greater brilliance and vividness of hue with, in general, less insistence on fastness to light; smoother flow, an especially important characteristic of carbon blacks. Coal-tar dye chemistry has contributed many widely used new pigments to the available lists in the past few years; notably phthalocyanine blues and greens, compounds derived from phthalimide and copper or other metals, more permanent and desirable than the old ultramarine and iron blues and greens. Such colors, when newly introduced, are often too expensive for general adoption in enamels, but the ink industry, spreading a pound of its product over a greater surface area, can usually afford to welcome them.

Many chemical problems are hidden in the small details of driers, anti-oxidants, lubricants, and surface-active agents which may make just the difference between an ink that works and one that doesn't. The affinity of the various compounds used in making printers' rollers (glue-glycerol, glue-sorbitol, rubber, synthetic elastomers) for solvents and resins is of great importance. Not only the ink manufacturers, but also the larger printing plants, now have chemical and physical laboratories constantly at work to discover the general laws and principles, and to improve the processes, of the printing art. At present the efforts of ink chemists, like those of others in many fields, are largely directed to finding suitable replacements for many materials temporarily scarce or unobtainable because of stoppage of imports or need in war work. Out of this enforced shifting may come new methods of processing and formulation which will lead to important advances in the art. The spread of the printed word depends on inks. And inks, depend on the ink chemist.

Ludwig Gattermann

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MOST CHEMISTS use names merely as convenient appellations for texts, laws, reactions, types of equipment. Usually no thought is given to the man whose name is so glibly employed. One of the duties of the historian of chemistry is to convert a name into a person.

To the older organic chemists, "Gattermann" signifies his *Die Praxis des organischen Chemie*, on which most of them cut their teeth. This guide to the preparation and ultimate analysis of organic compounds was published in 1894; it has gone through several translations and many editions. As revised by Wieland it is still in use. The younger organic chemists think of "Gattermann" as the useful modification of the Sandmeyer reaction in which copper powder takes the place of cuprous salt.

Ludwig Gattermann was born on April 20, 1860, at Goslar. His father, proprietor of a bakery, was able to give him a good education. The boy showed unusual talents for science and mathematics, and by his own efforts acquired an excellent knowledge of calculus. He fitted up a laboratory at home, and to the admiring audience of his schoolmates demonstrated the experiments he learned at school and others gleaned from outside texts.

He went to Heidelberg to begin his university training in chemistry but did not stay long. Bunsen, then long past the peak of his greatness, did not interest the eager young man. In 1882 Gattermann entered the laboratory of the Gewerbe Akademie in Berlin. Here, under Liebermann and his assistant, Jacobsen, he learned to make organic preparations. At that time, there were no printed organic manuals; students worked from a local set of well-tested directions. After these exercises were completed, the young chemist was sent to the literature to select a more difficult preparation, which he was expected to repeat according to the published procedure. Jacobsen, Gattermann's biographer,[1] wrote that he never taught a student who worked more adeptly and neatly. Gattermann's first paper came out of this laboratory. He later confessed that this modest contribution had so excited him that he could not sleep for a week. The Gewerbe Akademie, which later became part of the Technische Hochschule, was directed to the training of industrial chemists. Gattermann's interests were academic and though he was making excellent progress in this school he again transferred after one semester, choosing a university of his native province.

Gattermann was at Göttingen for six years. In 1885 he received his doctorate, with a pedestrian dissertation on a topic suggested by Hübner, the head of the Chemisches Institut. Hübner died in 1884, and was succeeded by Victor Meyer, who arrived early in 1885 accompanied by Sandmeyer, his lecture assistant. Gattermann had held the same post under Hübner, and was now instructed by Sandmeyer, who stayed only one semester, in all the details of Meyer's elaborate repertoire of lecture demonstrations. Had Gattermann anticipated that he was to be lecture assistant for six years he doubtless would have refused this important though subordinate post, but it proved to have a decisive effect on his career. This close contact ripened into intimacy, and he became Meyer's right-hand man in all manner of ways, particularly in connection with the extensive building operations at Göttingen and later at Heidelberg.

Meyer saw to it that Gattermann had time for scientific work, and provided him with assistants to do much of the experimental labor. In this Göttingen period fall some of Gattermann's important successes, such as his method of preparing aromatic carboxylic acids with the aid of $AlCl_3$ and urea (carbamyl) chlorides. Especially striking was his analysis of nitrogen trichloride. Meyer's lecture demonstrations with this devilishly explosive compound had led Gattermann to look into its history. He found that no real analysis of it had been accomplished, or even attempted. Unweighed samples of untested purity had been used to establish the N : Cl ratio. He conceived the bold plan of purifying the oil in the usual way by washing and drying it and then analyzing a weighed sample in the normal way. It is distinctly worth while to read his account of this work.[2] He showed that the action of chlorine on ammonium chloride ordinarily does not give a single material; only after prolonged treatment with this gas does the product correspond to the formula NCl_3. This spectacular research brought him considerable publicity, even in the daily press. One day a clipping from an English newspaper was passed around the laboratory; in it he was acclaimed "a hero of science." From then on, his close friends liked to use the nickname "hero."

He frequently worked on problems presented by the dye manufacturers, whose laboratories at that time were not the highly organized research institutions they now are. Summers were often spent in the dye works. This close connection, which lasted more than thirty years, was of great benefit to his students, whom he was thus able to place in good jobs.

In 1889 Meyer succeeded Bunsen at Heidelberg, and

[1] JACOBSEN, *Ber.*, **54A**, 115 (1921). For details of chemical instruction in the Gerwerbe Akademie see WALLACH, *ibid.*, **51**, 1136 (1918).

[2] GATTERMANN, *Ber.*, **21**, 751 (1888); see also MEYER, *ibid.*, **21**, 26 (1888).

took with him most of his assistants. Gattermann was made extraordinary professor, but still acted as lecture assistant. Not until 1892 was he able to devote his entire time to research and teaching. His achievements included the modification of the Sandmeyer reaction, the hydroxylation of anthraquinone, the electrolytic reduction of aromatic nitro compounds, the preparation of $AlCl_3$ by heating the metal turnings in a current of hydrogen chloride; the saponification of phenolic ethers by means of $AlCl_3$, the direct synthesis of aromatic aldehydes from the hydrocarbons and carbon monoxide in the presence of cuprous chloride; the preparation of hydroxylated aldehydes with the aid of anhydrous prussic acid. Concerning this reagent he wrote to Sandmeyer: "After you get accustomed to handling this material, it really is no more dangerous than alcohol." He recommended that the operator smoke while working with prussic acid because even traces in the air are then revealed by a characteristic taste. In the inorganic field he continued work on silicon begun at Göttingen. He prepared $SiCl_4$ by passing chlorine over the reduction mixture obtained from metallic magnesium and silica. The hexachloride is also obtained along with small amounts of the octachloride. The latter was used to prepare silico-mesoxalic acid $(H_4Si_3O_6)_x$.

His well-known *Praxis* was a product of his teaching at Heidelberg. He had no urge toward literary work and had to drive himself to put pen to paper. His style was curt and clear. This textbook, carefully distilled from his rich experience, was always referred to by him as the "cookbook," but its worth was appreciated in laboratories all over the world.

Gattermann was always anxious to learn. In 1897 he attended the course on physical chemistry, since he had never had a chance to become acquainted with this field, which had seen most of its development since his student days. He also sat with the students in a course on differential and integral calculus. Later, at Freiburg, he attended an undergraduate course in geology.

After Victor Meyer's tragic death, Gattermann acted as temporary head of the department until Curtius came as permanent chief in 1898. To him also Gattermann gave valuable assistance. A well-deserved call came to head the department at Freiburg and Gattermann left Heidelberg in 1900.

The rich harvest of original ideas had been largely gathered in. Though no less than 65 doctoral dissertations came from his Freiburg laboratory, they were for the most part, merely extensions of his previous studies. Administrative duties, possibly the beginnings of arteriosclerosis to which eventually he succumbed, domestic difficulties with his temperamental wife that led finally to a divorce, all kept him from the actual handling of materials, which so often had been his inspiration.

During and after the great war, assistants were scarce, so he took over a large part of the beginning laboratory instruction and also taught in the secondary schools. From this firsthand knowledge he was led to develop some modifications of analytical procedures and to devise new experiments for beginners. Scarcity of chemicals made economies necessary; he became one of the pioneers in the use of micro methods and equipment in beginning courses. His last public lecture was a demonstration of these new teaching devices.

Gattermann died on June 20, 1921. His influence will keep his name alive among chemists for many years to come.

Out of the Editor's Basket

IT IS welcome news that the plan to provide federal loans to technical students has at last been completed. Announcement was recently made by the U. S. Bureau of Education that five million dollars has been appropriated by Congress for this purpose.

Essential points of the student war loan program as developed by Commissioner Studebaker are:

Where to apply: Loans are made to students directly by colleges or universities.

Special conditions: Loans are available *only to students who are registered in* accelerated programs *in degree-granting colleges and universities and whose technical or professional education can be completed within two years,* in one of the following fields:

Fields of work: Engineering, Physics, Chemistry, Medicine (including veterinary), Dentistry, and Pharmacy.

Written agreement: The student agrees in writing (1) to participate, until otherwise directed by the Chairman of the War Manpower Commission, in accelerated programs of study in any of the authorized fields; and (2) to engage for the duration of the wars in which the United States is now engaged, in such employment or service as may be assigned by officers or agencies designated by the Chairman of the War Manpower Commission.

Scholarship: Students must attain and continue to maintain satisfactory standards of scholarship.

Need: Students must be in need of assistance.

Maximum loan: Loans shall be made in amounts *not exceeding tuition and fees plus $25 per month, and not exceeding a total of $500* to any one student during any 12-month period.

Security: Loans are to be evidenced by notes executed by student borrowers payable to the Treasurer of the United States.

Interest Rate: The rate of interest is $2^1/_2$ per cent per annum.

Repayments: Repayments of loans are to be made through the colleges, universities, or other agencies negotiating the loans, to be covered into the Treasury as miscellaneous receipts.

Cancellation: The indebtedness of a student shall be cancelled: (1) if before completing his course he is ordered into military service during the present wars under the Selective Training and Service Act of 1940, as amended; or (2) if he suffers total and permanent disability; or (3) in case of death.

● In the mobilization of manpower for the civilian war service of the Government, there is a continuing call for scientifically and technically trained men and women. Among those wanted are metallurgists and chemists. It is expected that more than a hundred metallurgists will be needed during the coming year in the Bureau of Mines, and there is a constant need for chemists in various branches of the Government. See Civil Service announcements.

● Using only a glass tube, a photocell, a light source, and a milliammeter, P. R. Kalischer, Westinghouse research metallurgist, can determine grain sizes of metallic powders as small as $^1/_{25,000}$ inch in about $^1/_{30}$ the time required for such an analysis. Since the quality of a metal produced by powder molding is dependent on the uniformity of the metal grains, the determination of the particle-size distribution is especially important.

Photocell and light source are mounted on opposite sides of the glass tube, and the output of the photocell is read by the milliammeter. To analyze a powder specimen, 1 g. of it is mixed with 100 cc. of acetone, to which a small amount of a wetting agent (isopropyl xanthate is one of the best) is added. The tube then is clamped between the photocell and the light source. As the particles settle, the liquid clears and transmits more light to the cell.

From timed readings of cell current, a time-opacity curve is plotted for that specimen. By comparing this curve with similar curves for standard powders of known size, one can determine both average particle size and relative quantities of grains of different sizes in the test specimen.

● With the release this month of *Selected Educational Motion Pictures: A Descriptive Encyclopedia*, an entirely new type of educational film catalog becomes available for teachers and administrators. This encyclopedia is obtainable (price $3.00) from the American Council on Education, 744 Jackson Place, Washington, D. C.

Of the thousands of films available to schools, only those are included which (1) have been reported as effective in the curriculum by teachers, (2) have a wide range of usefulness in the curriculum, (3) are nationally available, and (4) conform to minimum technical standards.

● Just as Pizarro, conqueror of Peru, once shod his horses with silver in an emergency, General Electric engineers are now using the precious metal instead of tin, copper, and other scarce materials in electrical apparatus.

The use of silver is saving huge quantities of tin at General Electric. In 1940 the company used approximately one million pounds of tin. This year, in spite of the fact that production has more than doubled, it is estimated that the amount of tin consumed will remain the same.

Silver is replacing tin in soft solders, alloys which require comparatively low temperatures in joining metals. Substitutions of silver for copper are being made in brazing alloys, which require high temperatures for joining metals.

It has been reported that the WPB already has effected a deal whereby silver has been loaned "for the duration" to an aluminum concern for busbars essential to production. The situation is complicated by legislation which requires the Government to buy domestic silver at 71.11 cents an ounce, more than double the world price of approximately 35 cents. Also, the sale of Treasury stocks is forbidden.

● A new type window of transparent plastic laminated with wire mesh which will withstand the explosion of a 150-pound bomb eight feet away has been developed for use in military construction and industrial plants in potential air-raid zones.

● An interesting booklet came to our attention the other day, entitled "Water Handbook," published by W. H. and L. D. Betz, Gillingham and Worth Streets, Frankford, Philadelphia, Pennsylvania, and obtainable for 50 cents postpaid. It consists of two parts, the first devoted to methods of analysis, and the second to the interpretation of water analyses. A number of applications to student use suggest themselves.

● Undergraduates in Harvard College and Radcliffe College may now enter an integrated five-year program leading to the Bachelor's degree at the end of the fourth year and the A.M. in teaching at the end of the fifth year. Decision to enter this program must be made at the close of the sophomore year. Nine semester hours in education will be taken in the junior and senior years; sixteen semester hours in education in the graduate year. Fields of concentration (majors) have been recognized in the teaching of the classics, English, fine arts, mathematics, modern foreign languages, music, the natural, or social, sciences.

● Mr. Jack De Ment, of Portland, Oregon, has sent us a description of a simple apparatus for demonstrating the fixation of atmospheric nitrogen by means of alpha radiation. A little radio thorium is used as the source of alpha rays, and is placed in a small capsule, which is, in turn, inserted into the bottom of an ordinary test tube. The tube is sealed tightly with a solid stopper which carries a fine glass rod or filament extending into the tube. On the end of the rod, or filament, is hung a small drop of a solution of diphenylamine in concentrated sulfuric acid (one part in 500). This reagent turns blue in the presence of nitrogen oxide. The capsule containing the radio thorium is tilted in such a way that the direct radiation cannot reach the reagent. In the course of from a few hours to two days, the reagent is said to show the presence of fixed nitrogen in the form of oxide. A control tube, similarly constructed but containing no radio thorium, is also used.

What's Been Going On

LARGE quantities of synthetic resins and plastics, drying oils, and solvents, requisite for war manufacture, are saved by the substitution of soybean and casein proteins in industrial processes. War effort demands huge amounts of such solvents as ethyl alcohol, employed in smokeless powder, coal-tar solvents like toluol, necessary in making TNT, and chlorine, an intermediate in the processing of war gas and smoke screens. By permitting the use of emulsion processes instead of solvents in non-war industries, these agricultural proteins release critical chemicals for more important purposes.

The soybean is also a great help in offsetting the results of reduced imports of oils from the Far East. Before Pearl Harbor, America was getting well over a billion pounds of fats and oils a year from areas now dominated by Japan. This year, according to the Bureau of Industrial Conservation, approximately a billion pounds of domestic soybeans will be produced, an increase of 50 per cent over last year's production. The oil is usually removed from the bean either by solvent extraction or mechanical pressing with a press called an "expeller."

Only about 15 per cent of the soybean weight is recovered as oil. Allowing for waste, about 80 per cent of the separation process is a high-protein meal, from which a vegetable equivalent of casein can be produced. The soybean oil goes into a variety of edible products, as well as into industrial uses. Figures from the Bureau of Census showed a total factory consumption of 464,000,000 pounds of soybean oil in 1941. Of this amount, 216,000,000 pounds went into vegetable shortening, 76,000,000 pounds into oleomargarine, 48,000,000 pounds into other edible products. Soap manufacture took 25,000,000 pounds; paints and varnishes, 42,000,000 pounds; linoleum and oil cloth, 8,000,000 pounds; and miscellaneous industrial uses, 23,000,000 pounds.

The soybean meal, half protein, that remains when the oil is pressed out is used principally as a stock feed, but it also serves as a raw material for making many other products. Several hundred million pounds of soybean flour will be produced for human consumption this year, and many million pounds of the inedible grades of soybean meal will be used as fertilizer. The 1942 soybean crop is estimated at 175,000,000 bushels, grown chiefly in the middle west. Indiana, Illinois, Iowa, and Ohio are the principal growing areas. Soybean acreage has increased many-fold in the past ten years and this legume is rapidly becoming one of the most important agricultural crops in the country. A large proportion of the soybean is consumed in the field by cattle, thus constituting an important intermediate factor in the production of milk and meat.

An expansion in the use of soybean and casein protein as replacement for tapioca starch, as a film-forming agent in paints and adhesives, as an emulsifying agent and stabilizer is suggested by the Bureau of Industrial Conservation as a means of saving other chemical substances. Other instances in which these proteins may be substituted include the manufacture of laminated fiber-board, textile dressings, synthetic fibers, and glue.

TO GIVE the metal proper characteristics, steel is often heated in an atmosphere of highly purified hydrogen that is practically free from moisture and oxygen. Ordinarily, to measure moisture in the gas where dew points are less than 0°C., a cooled and polished metal plate is inserted in the gas stream and the temperature noted when condensation of moisture first occurs. However, below −40°C. this method becomes largely guesswork and even skilled testers disagree on values of the same

Courtesy of Westinghouse

ELECTRONIC CONTROL GUARDS FURNACE ATMOSPHERE FOR TREATING STEEL

gas. An electronic method, developed in the Westinghouse laboratories, insures reliable and accurate determination of moisture and oxygen content in hydrogen (or disassociated ammonia) gas.

In operation, the gas flows through a 2-element tube containing a tungsten filament and plate. Electrons flying from the hot filament to the plate continually bombard the gas. If the gas is pure, dry hydrogen, all the electrons reach the plate. But any oxygen or water vapor in the gas will immediately pick up some of the electrons and form negative ions, thereby reducing the electron current. This change of current in the plate circuit indicates the degree of impurity in the gas.

RECENT BOOKS

A TEXTBOOK OF ELEMENTARY QUALITATIVE ANALYSIS. *Carl J. Engelder*, Ph.D., Professor of Analytical Chemistry, University of Pittsburgh. Third Edition. John Wiley and Sons, Inc., New York City, 1942. x + 344 pp. 15 × 23 cm. $2.50.

LABORATORY RECORD BOOK OF QUALITATIVE ANALYSIS. *Carl J. Engelder*, Ph.D., Professor of Analytical Chemistry, University of Pittsburgh. Second Edition. John Wiley and Sons, Inc., New York City, 1942. 91 pp. 15 × 23 cm. $1.25.

The new edition of this textbook on qualitative analysis differs from its predecessors in many respects. The theoretical part has been expanded so as to include such concepts as atomic structure, types of valence bonds, the Werner theory, the Brønsted theory of acids and bases, the doctrine of complete ionization, redox equations, and the electrochemical theory of oxidation-reduction, including the calculation of equilibrium constants. Part II, which deals with the reactions of the cations, has been enlarged by introducing, before the experimental work on each ion, a discussion of its properties and reactions. New methods of separation and detection have been included in several cases. In Part III, dealing with the analysis of the anions, the new procedure of Dobbins and Ljung [J. CHEM. EDUC., **12**, 586–8 (1935)] has been followed, in which the anions, in slightly basic medium, are divided into groups, using $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Zn(NO_3)_2$, and $AgNO_3$ as group reagents.

As in the previous editions, the procedures are on the macro scale. With the usual exceptions, organic reagents are not used. The book is attractive mechanically, and unusally free from typographical errors.

Appearing as a companion volume to the textbook is a second edition of the LABORATORY RECORD BOOK OF QUALITATIVE ANALYSIS, by the same author. This notebook is based on the new edition of the textbook, and contains in skeleton form blanks to be filled in by the student, including equations to be balanced. The pages for reports on unknowns are perforated so that they may be detached and turned in for correction and grading.

J. H. REEDY

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OUTLINES OF FOOD TECHNOLOGY. *Harry W. von Loesecke*, U. S. Department of Agriculture, Winter Haven, Florida. Reinhold Publishing Corporation, New York City, 1942. 505 pp. 84 figs. 16 × 24 cm. $7.00.

The purposes of the book as stated by the author are to outline the processes used in the modern food industry and to describe briefly and without detail the more important food processes. These objectives are well achieved. An abundant amount of information is brought together, material that is not to the reviewer's knowledge now assembled elsewhere in a single volume. Although one frequently wants additional information, only an outline has been promised; footnote references are generously provided, however, within the pages of each chapter and one can refer to them for further detail.

The table of contents gives an indication of the material covered: The Tin Can and Glass Container; Fruits and Their Products; Canning of Vegetables; Dairy Products; Meat, Meat Products and Poultry; Fish and Shellfish; Grains and Their Products; Edible Fats and Oils; Sugars and Starches; Nuts; Spices, Relishes, Essential Oils, and Extracts; Beverages; Confectionery, Jams, Jellies, Preserves and Certified Dyes; Storage and Marketing of Fruits and Vegetables; Preservation of Foods by Freezing.

The individual chapter headings, however, cannot be relied upon to give a complete picture of the contents within the chapter. Unfortunately this occasionally gives rise to confusion for continuity is sometimes broken by the insertion of information which, although always interesting, is related to rather than essential to the subject at hand. For example in chapter 1, "The Tin Can and the Glass Container," the discussion of lacquered cans is interrupted by a description of swells and flippers and inspection of the container, whereas the discussion is resumed about six pages further on; chapter 3, "The Canning of Vegetables," includes pickles, potato chips, tomato products such as catsup and chili sauce, and also the dehydration of vegetables; chapter 7, "Grains and Their Products," includes a discussion of baking powders and the manufacture of yeast which is discussed several pages after bread.

Continuity is broken rather frequently by the placement of tables in rather unfortunate positions. Also, Fruits and Their Products and The Canning of Vegetables appear as chapters 2 and 3, respectively, separated a considerable distance from Jams, Jellies and Preserves, Storage and Marketing of Fruits and Vegetables, and Preservation of Foods by Freezing, which are discussed in chapters 13, 14, and 15, respectively.

There are relatively few errors for such a large volume, but some appear: ethers for esters, amino for amino acid, (000) instead of a page reference, maltrose for maltose, 200°F. for, presumably, 220°F., and also the failure to include in a table all the things given in the heading. At times an unfortunate arrangement of words gives an incorrect impression, as, for instance, that the pouring of liquid into cans and sealing are parts of pasteurization, that both glucose and fructose are obtained from maltose, and that the process is inversion.

For the most part, however, the material is clearly presented, well selected, and above all exceedingly interesting. The scope is broad and the area is well covered. At times a gratifying amount of detail is included. A real contribution has been made to the field of food technology in the assembling and presenting of this material.

MARION C. PFUND

CORNELL UNIVERSITY
ITHACA, NEW YORK

PRACTICAL PHYSICAL CHEMISTRY. *Alexander Findlay*, Professor of Chemistry, University of Aberdeen. Seventh Edition. Longmans, Green and Co., London, New York City, Toronto, 1942. x + 335 pp. 124 figs. 14 × 21.5 cm. $3.00.

This well-known book, which has been through six editions and many reprintings since 1906, now appears revised and amplified. The general arrangement remains the same. It is not an exhaustive treatise but aims to give a good, fundamental training in physical chemical technics. Numerous experiments and practical applications provide ample latitude for diversity of assignment.

The following subjects are new to this edition: Thyratron relays; refrigeration for thermostats; improved vapor density apparatus; the maximum bubble pressure method for surface tension; absorption spectra of colored solutions; the antimony and tungsten electrodes; boiling point curves for binary liquid systems; equilibrium curves in three-component systems. Two new tables are noted in the appendix—values of g and the ion product of water versus temperature. Table II in the appendix has quinoline misspelled. Thirty-two tables of useful data are scattered throughout the text. Literature references are sufficient but not extensive.

The general excellence and desirability of this book cannot be more forcefully stated than this—probably more chemists have been "raised" on Findlay than any other comparable work. The seventh edition is a real improvement.

MALCOLM M. HARING

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THE PHYSICAL EXAMINATION OF METALS. Volume II. Electrical Methods. *Bruce Chalmers*, D.Sc., Ph.D., F.Inst.P., Physicist, Tin Research Institute; and *A. G. Quarrell*, A.R.C.S., Ph.D., F.Inst.P., Lecturer in Metallurgy, University of Sheffield. Longmans, Green and Company, New York City; Edward Arnold and Company, London, 1941. viii + 280 pp. 112 figs. 13.5 × 21.3 cm. $6.00.

Electrical technics in the examination of metals have been collected in this volume, and the authors have attempted to indicate the scope and limitations of each of the methods described—doing so, where possible, by reference to successful applications. At the same time, no attempt has been made to include a complete bibliography of the subject. The topics covered include magnetism, electrical measurements, X-ray diffraction, the diffraction of electrons, the electron microscope, and radiography. The appendixes include data on electrolytic brightening, the crystalline structure of metals, the crystal systems, change of axes, the rhombohedral system referred to hexagonal axes, the angle between two planes, monochromatic radiations used in X-ray analysis, radiation for Laue photographs and wave length of high-speed electrons. The volume should prove useful not only to those concerned with the development of new or more specialized tests for metals and metallic components, but also to those who have not heretofore had this information in readily available form.

CHEMICAL ENGINEERS' HANDBOOK. *John H. Perry*, Ph.D., Editor, E. I. du Pont de Nemours and Company; Member, American Institute of Chemical Engineers, American Chemical Society, Franklin Institute, American Society for Advancement of Science, Society for the Promotion of Engineering Education. Second Edition. McGraw-Hill Book Company, Inc., New York City and London, 1941. xviii + 3029 pp. 1469 figs. 12.2 × 17.8 cm. $10.00.

An encyclopedic yet handy reference book is this standard work, which should be available to every practicing engineer and student in chemical engineering and related fields. Thorough revision and expansion have produced the second edition, which contains the following new material: table of the physical and chemical properties of inorganic chemical compounds; section on solvent extraction; section on shotting, granulation, flaking, and sprays and spraying; section on bulk packaging of materials; section on sublimation; chapter on technical calculations; chapter on thermodynamics with a new table of the free energies of chemical compounds; chapters on such mechanical separations as electrostatic, electromagnetic, sink-and-float, flotation, etc.; table of the various gages for wire and sheet metal; tables of pipe and tubing. A new and more comprehensive index has been added.

MICROMETHODS OF QUANTITATIVE ORGANIC ANALYSIS. *Joseph B. Niederl*, Ph.D., Associate Professor of Chemistry, New York University Graduate School and Washington Square College, and *Victor Niederl*, Teaching Fellow, New York University, Washington Square College. Second Edition. John Wiley and Sons, Inc., New York City, 1942. xiii + 347 pp. 62 figs. 15 × 23 cm. $3.50.

This is the second edition of a laboratory text which appeared in 1938 and has been of real service in the rapidly expanding field of microanalysis of organic compounds. Like the earlier edition, which was reviewed in J. CHEM. EDUC., **15**, 349 (1938), the text first covers the use of the balance and general methods of microchemical technic. Following this are discussions of the methods of elementary analysis with stress on the determination of nitrogen, carbon, hydrogen, halogens, and sulfur. The next sections are concerned with molecular weight determinations and structure analysis, and a useful appendix gives practical suggestions for installing a microanalytical laboratory and teaching the subject.

In this new edition modifications in a number of procedures are included and the literature references have been brought up to 1941. Among these changes may be mentioned the expansion of the chapter on the balance, the recommendation of potassium biiodate as a standard for acidimetry, and the discussion of new methods of molecular weight determination.

The inclusion only of well-tested procedures and the detail and clarity of the directions make this book a valuable guide to those who are using or teaching microanalytical methods. It has been possible to carry out these procedures successfully with the aid of the book alone. One might prefer for teaching purposes that directions for calculations were not so mechanically given since the student taking this work should be able to calculate results without this aid. This reviewer wishes that more attention had been given to the boric acid modification of the Kjeldahl determination.

The authors call attention to the fact that this edition is published at the thirtieth anniversary of the introduction of the subject by Pregl and note the rapid progress made in this branch of science, as indicated by literature citations of over a thousand references. Certainly the authors themselves are entitled to much credit for the significant part they have played in this rapid development.

LUCY W. PICKETT

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SOUTH HADLEY, MASSACHUSETTS

CHEMICAL SOLUTIONS. REAGENTS USEFUL TO THE CHEMIST, BIOLOGIST, AND BACTERIOLOGIST. *Frank Welcher*, Assistant Professor of Chemistry, Indiana University. D. Van Nostrand Company, Inc., New York City, 1942. vii + 404 pp. 15 × 23 cm. $4.75.

This useful book for the practicing chemist and teacher of chemistry contains information on reagents and solutions, including (1) the uses of each solution, (2) the procedure for use of each in all cases where this is practicable, (3) a list of those substances which interfere in making special tests, (4) the sensitiveness of test reagents, and (5) general remarks regarding the keeping qualities, methods of storage, etc., of the various reagents. In addition to this practical information, references have been included for each solution in all cases where a useful citation is available—very often not to the original literature, but to standard and easily available books and periodicals, generally in English. Solutions contained in the volume are those commonly used in routine experimental work in organic chemistry, biochemistry, metallurgy and metallography, food chemistry, bacteriology, gas and fuel analysis, college and high-school instruction in chemistry, general testing, water analysis, etc. Special solutions used only in certain rare experiments, and trade formulas do not appear. The book is completely practical and should prove indispensable for handy reference.

WOOD TECHNOLOGY. CONSTITUTION, PROPERTIES AND USES. *Harry Donald Tiemann*, M.E., M.F., Senior Wood Physicist, U. S. Forest Products Laboratory, Lecturer in Forest Products, University of Wisconsin, Senior Member, Society American Foresters, Charter Member, International Association of Wood Anatomists, Member Sigma Xi. First Edition. Pitman Publishing Corporation, New York City, 1942. x + 316 pp. 85 figs. 15 × 23 cm. $3.50.

The purpose of this book is to summarize, not only for the student but for everyone interested in the use of wood, the large amount of information on the physiology, anatomy, description and identification, chemical utilization, physical and mechanical properties, seasoning and drying, and the so-called "pathology" and preservation of wood. The result is a comprehensive yet brief and simple presentation of the old and some new in wood technology by a world authority with 35 years' experience in research on wood, mostly at the Forest Products Laboratory conducted by the U. S. Forest Service at Madison, Wisconsin. The book is adequately illustrated by excellent and well-selected photographs and photomicrographs, and a few line drawings. Each chapter ends with a list of references to literature. For the chemist, the information is fundamental rather than detailed.

WALTER H. SNELL

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CHEMICAL INDUSTRIES' BUYER'S GUIDEBOOK NUMBER. *Walter J. Murphy*, B.S. (F.A.I.C., Editor; *James M. Crowe*, B.S. in Ch.E., Associate Editor; *M. Crawford, C. Hubert*, and *V. DeLea*, Assistant Editors. Seventeenth Annual Revision. Tradepress Publishing Corporation, New York City, 1941. 736 pp. 22 × 29.2 cm. $1.50.

This annual volume has been expanded in the latest revision through the addition of a section on all types of equipment, apparatus, containers, and packaging and labeling machinery. The seventeenth edition also contains a new Technical Section, supplying engineering data for easy reference. The buying guide has information on where to buy raw materials, chemicals, industrial chemical specialties, equipment, and containers. Technical data such as formula, physical and chemical properties, uses, shipping containers, shipping regulations, and tariff rates provide chemists and chemical engineers as well as buyers with pertinent information. Changing conditions due to government regulations and conversion of industries to war work may well have made parts of the buying guide obsolete.

Other sections provide a geographical list of all chemical manufacturers, jobbers, and distributors; an alphabetically arranged list of equipment and container companies; a five-year comparison of chemical prices; a list of associations allied with the chemical industry; and a checklist of over 20,000 brand and trade names identifying the product and the maker.

PHYSICAL CHEMISTRY. *Frank Thomson Gucker, Jr.*, Associate Professor of Chemistry, Northwestern University, and *William Buell Meldrum*, Professor of Chemistry, Haverford College. First Edition. American Book Company, New York City, 1942. xii + 683 pp. 262 figs. 14 × 21.5 cm. $4.00.

This book is designed as a text for an elementary course in physical chemistry. All of the customary topics are adequately covered. The development of the material is unusually full and clear. Only an elementary knowledge of mathematics is required for an understanding of the text. Equations such as the Clausius-Clapeyron equation are introduced at various points but their derivations are left to the last chapter (Thermodynamics and Mathematical Derivations). There are several chapters of particular interest to men going into medicine (Hydrogen Ion Concentration and pH, Enzymes). By a proper selection of chapters this book could be used for a one-semester course in physical chemistry for premedical students.

The book is well printed. The tables and diagrams are clear. From time to time there are interesting biographical footnotes. At the end of each chapter are numerous problems (without answers) and a useful reading list. At the end of the book are four pages of symbols with a notation of the page where each is introduced or defined, and a 23-page index.

This book should be an excellent text for courses where a strict mathematical treatment is not necessary or desired.

WILLIAM ROOT

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BRIEF COLLEGE CHEMISTRY. *Leon B. Richardson* and *Andrew J. Scarlett*, Professors of Chemistry, Dartmouth College. Henry Holt and Company, Inc., New York City, 1942. vi + 385 pp. 128 figs. 15.5 × 23.5 cm. $3.00.

The authors have prepared this book to meet the needs of students enrolled in brief courses in general chemistry. Such courses are quite common, particularly in the larger institutions, and are often designed for students of agriculture, home economics, engineering, etc. Suitable textbooks for such courses are not numerous, as the reviewer can well testify from an extensive experience in teaching such courses. The authors have recognized this need, and have stated the case very well in their preface. "The instructor in these courses is usually compelled to choose between two classes of texts; those which are highly elementary, and those which are so extensive that time is lacking for a consideration of a large portion of their content. If the first alternative is adopted, the material is so superficial as not to be adapted to students of college grade. If the second is selected, the fact that a large amount of the text must necessarily be omitted often leads the student to form the impression that he is missing much that should be included. . . ."

A definite effort has been made to prepare a new text, and not an abridged edition of the authors' well-known "General College Chemistry" (*cf.* J. CHEM. EDUC., **17**, 500 (1940)). "No concessions have been made to facile treatment, or to restriction of the more difficult topics (if that material is deemed to be important) merely because it is difficult and the time is short. The book is written with a view to making it possible for a college student of no previous chemical training to obtain an adequate idea of the factual basis of general chemistry, illuminated by such understanding of its theoretical aspects as to enable him, within limits, to explain to himself the fundamental reasons for the changes and reactions which he studies."

The first five chapters include a fairly thorough discussion of fundamental conceptions, quantitative relations, valence, the periodic system, the structure of atoms, radioactivity. The remaining 27 chapters cover the topics usually found in general chemistry texts including an excellent elementary treatment of electrochemistry, and the last two chapters are devoted to organic chemistry. The exercises and problems (with answers) are, in many cases, different from those usually found in general chemistry textbooks. Some of them are, perhaps, beyond the range of the average student.

The concepts of atomic structure and the Brønsted theory of acids and bases are well developed and consistently applied throughout the text. The diagrams are unusually clear and well drawn, and the numerous photographs of plant installations are modern and well chosen, *e. g.*, incendiary bombs (Figure 96) and plexiglas (Figure 127). As in all new editions, minor errors appear, *e. g.*, on p. 63, section 66, the reference (43, 2) should be (43b). On p. 105, in the third equation, the gram-atomic weight of zinc is incorrectly stated as 75.37 g. Incidentally, the numbered sections will be a distinct help to both student and instructor. The book is very attractively bound.

For the dull or careless student, or for the student with a mediocre training in high-school science, this text will be a large order. The alert, conscientious student will find the book very stimulating, and a challenge to his best efforts. To instructors who are anxious to present their courses in accordance with the recent developments in the field, this book is highly recommended.

A. J. CURRIER

STATE COLLEGE
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GENERAL CHEMISTRY PROBLEMS. *Edwin C. Markham* and *Sherman Smith*, University of North Carolina. Reynal and Hitchcock, Inc., New York City, 1942. vi + 239 pp. 8 figs. 19.7 × 26.3 cm. $1.25.

According to the authors, "in general, the attempt has been made to prepare an adequate background of text for each separate type of problem. These brief discussions employ an experimental approach, using diagrams wherever possible, in order to enable the student to visualize the problem in its physical rather than its purely mathematical aspects." Each set of problems is preceded by one or more illustrative examples which serve to emphasize form in the solution of each particular problem type. The proper identification of dimensions for all quantities is demonstrated as a useful technic. An exercise is included, in most cases, which calls upon the student to explain the logic of each step in the solution of a typical problem. The solution of problems by the method of proportion has been avoided in general.

The introductory sections of the book on units and dimensions, significant figures, exponential numbers, and logarithms are unusually extensive. Space for the solution of each problem is provided, separate from the text so that the answer sheets may be removed for grading and then reinserted. The book should prove useful for extra practice in the problem solving which is an essential part of a student's training.